

MAHARISHI COLLEGE OF

NATURAL LAW

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Semester - I

Unit - II Periodicity of Elements.

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Periodicity of Elements

Modern Periodic Law

The physical and chemical properties of elements are the periodic function of their atomic number.

Periodicity

The recurrence of elements with similar properties after certain regular interval when these are arranged in the increasing order of their atomic number is called periodicity.

Properties of elements get repeated after intervals of 2, 8, 8, 18, 18, 32 \rightarrow Magic No.

Causes of Periodicity : Recurrence of similar electronic configuration.

Modern IUPAC Periodic Table - Long or Extended form of the Periodic Table. (Bohr's Table)

Modern Periodic Table \rightarrow Discovered by Moseley.

According to this law : "The physical and chemical properties of elements are the periodic function of their atomic number. i.e. when elements are arranged in the increasing order of their atomic number, similar elements are repeated at regular interval.

* Modern Periodic Table \rightarrow Improved by Mendeleeff.

* Effective Nuclear Charge : The physical and chemical properties of elements depend on their electronic configuration, so it is important to find out the effect of nucleus on electron.

Actually nuclear charge (Z) is different from effective nuclear charge.

Shielding constant : (σ)

$$E_n(\sigma) = -\frac{2\pi^2 m e^4 Z^2}{n^2 h^2}; \quad E_n \propto \frac{Z^2}{n^2} \quad \checkmark$$

n = Principal quantum number, and
 Z = Actual nuclear charge (= Atomic No.)

Thus, the energy of the outermost electron will increase rapidly with increase in principal quantum number.

If E_n of H is the energy of the hydrogen atom = 13.6 eV
Ionisation Energy of He (E_{He}) = ~~$4 \times E_H$~~ $4 \times 13.6 \text{ eV}$
= $4 \times 13.6 \text{ eV} = 54.4 \text{ eV}$

E_{He} observed = 24.4 eV.

$$[{}^2_2\text{He} = 1s^2, Z=2, n=1 \text{ and } \frac{Z^2}{n^2} = \frac{2^2}{1^2} = 4]$$

Q. $E_{Li} = ?$

$$[{}^3_3\text{Li} = 1s^2 2s^2, Z=3, n=2] \quad \left(E_n = \frac{Z^2}{n^2} = \frac{3^2}{2^2} \right) = \frac{9}{4}$$

$$E_{Li} = \frac{9}{4} E_H = 30.5 \text{ eV}$$

$$E_{obs} = 5.4 \text{ eV}$$

Q $E_{Be} = ?$

$$[{}^4_4\text{Be} = 1s^2 2s^2] \quad Z=4, n=2 \quad \left(E_n = \frac{Z^2}{n^2} = \frac{4^2}{2^2} = \frac{16}{4} \right)$$

$$E_{Be} = \frac{16}{4} E_H = \frac{16}{4} \times 13.6 = 54.4 \text{ eV}$$

$$E_{obs} = 7.32 \text{ eV}$$

So, the effective of reduction of force of attraction by the same nucleus and valency electron is called shielding const.

→ The extent to which the orbital of a shell increases with the lower quantum no. of orbital is called penetration of orbital.

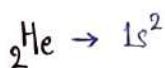
→ The presence of one node and an internodal max. in 3p orbital and the presence of 2 nodes and 2 internodal max. in 3d orbital, which will be affected more by the nucleus as compared to 3d orbital having no node and internode.

Slater's Rule

Calculation

- (i) He gave idea about calculation of σ
first write down the electronic configuration of element and group in the order.
- (ii) Electrons present in a group which are right side to the ns np don't contribute to the screening constant.
- (iii) All the other electron in the ns np group which has one electron less shield the valence e^- to an extent of 0.35
- (iv) For an electron in 1s orbital contribute 0.30 from other single e^- .
- (v) All the electrons in the $(n-1)$ shell will shield to an extent of 0.85
- (vi) Other e^- in $(n-2)$ will shield to an extent of 1.0
- (vii) All the e^- present in the group which are on the left of nd or nf shield the valence e^- by 1.0

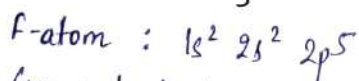
eg.



Value of σ for $1s^1$ (one e^- less than group e^- i.e., $(2-1=1)$ of He-atom = $1 \times 0.30 = 0.30$

$$\text{Effective Nuclear Charge } Z^* = Z - \sigma = 2 - 0.30 = 1.70$$

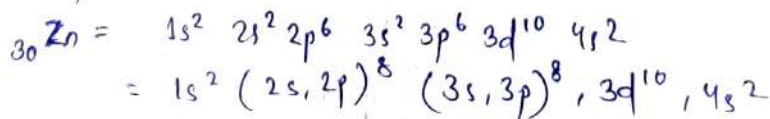
Q. Find the shielding constant of 2s or 2p e^- in fluorine atom.



- (i) Grouped electronic configuration is $(1s)^2 (2s^2, 2p)^7$.
 - (ii) Electron present in a group right to 2s and 2p is 0. (\because no group at 2s)
 - (iii) Shielding effect of $6e^-$ (i.e. of $1e^-$ less) using 0.35 value for each $e^- = 6 \times 0.35 = 2.10$
 - (iv) No. of e^- in $(n-1)^{\text{th}}$, i.e., $(2-1)$ or first shell = 2.
 \therefore Shielding effect of $2e^-$ using 0.85 value for each $e^- = 2 \times 0.85 = 1.70$
- \therefore Total value of ' σ ' for 2s or 2p $e^- = 2.10 + 1.70 = 3.80$

Q. Find shielding constant and effective nuclear charge of

(i) 3d- e^- and (ii) 1s e^- in zinc ($Z=30$).



(ii) 1s electron in zinc ($Z=30$)

$$\sigma \text{ for } 1s \text{ of } Zn_{30} \text{ atom} = 1 \times 0.30 = 0.30$$

effective nuclear charge,

$$Z^* = Z - \sigma = 30 - 0.30 \\ = 29.70$$

Penetration of orbitals

The extent to which one orbital of a shell interact with the lower quantum no. orbitals is called penetration of orbital.

Application of Slater's Rule.

It helps to solve the chemical problems such as

(i) Why a cation is smaller than its parent ion.

(ii) Anion is larger than its parent ion.

(iii) Why ns orbital is filled first ~~into~~ $(n-1)d$

(iv) While forming cations of transition element 4s \bar{e} are lost prior to 3d \bar{e} .

(v) It explains successive ionisation energy of elements.

(vi) Atomic and ionic size of elements of s and p block increases and decreases resp. in a group.

(vii) It explains Aufbau rules.

Merits or Limitation

(i) It is not reliable for bigger atom. (heavier element)

(ii) It is said that the \bar{e} present in s, p, d and f subshell shield the outer end shell \bar{e} ~~with~~ with equal contribution but it is not explained by Slater's rule.

(iii) The screening effect of 's' orbital should be more than 'p' orbital but according to Slater 's', and 'p' orbital of same shell are grouped together.

Atomic Radius

Distance from nucleus to outer most \bar{e} . (Unit - \AA)

It is difficult to calculate the exact atomic radius because an atom is unstable and can't be isolated to get its radius.

Heisenberg's uncertainty Principle.

According to Heisenberg's uncertainty Principle, if a measurement of the position of a particle is made with uncertainty Δx and a simultaneous measurement of its x comp. of momentum is made with uncertainty Δp_x , the product of the two uncertainties can never be smaller than

$$\Delta x \cdot \Delta p_x \geq \frac{h}{2}$$

Covalent Radius.

Ex. H_2, F_2 ; So for homoatomic molecule, the covalent radius is the distance b/w the two nucleus divided by 2

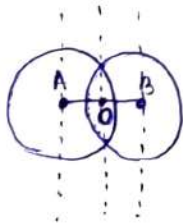
$$\text{eg. } C-C \rightarrow 0.77 \text{ \AA}$$

$$H_2 \rightarrow 0.37 \text{ \AA}$$

$$O_2 \rightarrow 1.17 \text{ \AA}$$

→ Heteronuclear molecule such as

Covalent single bond radius for A and B is difference between the bond length of AB.



Ionic Radius

It is the distance from the nucleus of that ion upto which it has its influence in ionic bond.

The size of Na^+Cl^- , Na^+ is 95 pm and Cl^- is 181 pm

The inter-nuclear distance of cation and anion in a ionic crystal in a X-ray crystallography. So to understand the concept of ionic crystal radius following assumption:

- (i) Existence of ion in solid compound.
- (ii) Correct division of the inter-nuclear distance b/w cation and anion.
- (iii) Additivity of ionic radii.

Characteristics	s-block	p-block	d-block	f-block
(i) Oxidation state	+1 / +2	Variable 0-5	Variable 0-5	+3, +4, +5, +6 0-5
(ii) Atomic and Ionic Radii	moving down the group size increasing	Decreases on moving across the table left to right	Decrease in a series with increase in atomic no.	decreases from lanthanum to lutetium
(iii) Ionisation Enthalpy	Moving down the group size increases	Increases on moving left to right	Increase with the increase in atomic no. up to Fe	Insignificant change in 1st and 2nd ionisation energy due to shielding effect.
(iv) General electronic configuration	ns^{1-2}	$ns^2 np^{1-6}$	$(n-1)d^{1-10} ns^{0-2}$	$(n-2)f^{0-14} (n-1)d^{0-1} ns^2$
(v)	Strong Reducing agent	Strong oxidising agent	Some are oxidising Some are reducing	Some - oxidising others - reducing
(vi) Melting and Boiling point	Decreases on moving from top to bottom	Decreases up to Gallium then increases	Increases and then decreases with increase in atomic no.	Increases then decreases.
(vii) mostly metals	mostly non-metal and metalloids	mostly non-metal and metalloid	Transition elements	Inner transition element

Ionic Radii : It increases with increase in atomic no. with in a group. The increase in ionic radii is quite rapid as we move from Li^+ to Na^+ and Na^+ to K^+ but from K^+ to Rb^+ and from Rb^+ to Cs it is not quite rapid.

Variation in a period : With in a period the radii of cation of normal elements of group I, II and XIII decreases with increase in atomic no. and due to increase in nuclear charge.

But for anions of group 16 and 17 the atomic size decreases as we move along the period so as the ion decreases.

Ionic Radii can be calculated by Pauli's Method.

for NaCl

$$\frac{r_{\text{Na}^+}}{r_{\text{Cl}^-}} = \frac{Z_{\text{Cl}^-}}{Z_{\text{Na}^+}}$$

for NaF

$$\frac{r_{\text{Na}^+}}{r_{\text{F}^-}} = \frac{Z_{\text{F}^-}}{Z_{\text{Na}^+}} = \frac{4.5}{6.5} = 0.69 \text{ \AA}$$

from the experiment

We already know that $r_{\text{Na}^+} + r_{\text{F}^-} = 2.31 \text{ \AA}$, determined from X-Ray studies of NaCl.

$$\text{Now } \frac{r_{\text{Na}^+}}{r_{\text{F}^-}} = 0.69 \Rightarrow r_{\text{Na}^+} = 0.69 \times r_{\text{F}^-}$$

$$\text{So } 0.69 \times r_{\text{F}^-} + r_{\text{F}^-} = 2.31$$

$$\Rightarrow 0.69 \times r_{\text{F}^-} = 2.31 - r_{\text{F}^-}$$

$$\Rightarrow 0.69 = \frac{2.31 - r_{\text{F}^-}}{r_{\text{F}^-}} = \frac{2.31}{r_{\text{F}^-}} - 1$$

$$\Rightarrow 1.69 = 2.31 / r_{\text{F}^-}$$

$$\Rightarrow r_{\text{F}^-} = 2.31 / 1.69 = 1.36$$

$$r_{\text{Na}^+} = 0.95$$

Ionisation Energy : The amount of energy required to remove an e^- from outermost electron shell of an atom/neutral gaseous atom.



$$I.E_1 \ll I.E_2 \ll I.E_3$$

The second ionisation energy as compared to 1st I.E

Factors affecting I.E

Atomic Size : $I.E \propto \frac{1}{\text{Atomic Size}}$

According to Coulomb's Law the attracting pull of nucleus on the outer e^- decrease and become easier to knock out the e^- from the outermost orbit of an atom.

Nuclear Charge : The force of attraction ~~to the~~ and an outer most e^- increases with increase in nuclear charge.

No. of e^- in the inner shell : The larger the no. of e^- in the inner shell the smaller is the I.E. This effect is k/a ~~the~~ screening effect or shielding effect.

Penetration effect or ~~the~~ effect of removal of s, p, d, f e^- from the same energy shell ($n=4$)

~~Ionisation energy~~

Methods of evaluation of Ionisation Energy

→ Spectroscopic Technical methods

→ It can also be measured by discharge tube containing gas vapour at low pressure.

Then the discharge tube is connected to a source of current. The potential difference is gradually increased and a stage ~~reaches~~ reaches when a sudden flow of current occurs at a particular voltage applied.

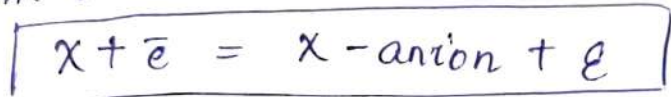
→ This is the 1st ionisation energy when the gas is ionised.

eg. Sodium (Na^+) is $\rightarrow 496 \text{ kJ/mol}$.

Application

1. Determination of valence \bar{e} in an atom.
2. Reactivity order of elements can also be determined by I.E value.
3. Reducing power prediction.

* Electron Affinity: It is defined as the amount of energy released when an \bar{e} is added to a gaseous isolated atom or ion.



Greater the energy released by taking the extra electrons; the greater is the \bar{e} affinity.

- \rightarrow Variation in a period: Increases (L to R)
- \rightarrow Variation in a group: Decreases (T to Bottom)

* Electron affinity of Beryllium / ~~Na~~ ($1s^2, 2s^2$)
 Mg ($1s^2, 2s^2, 2p^6$)
N

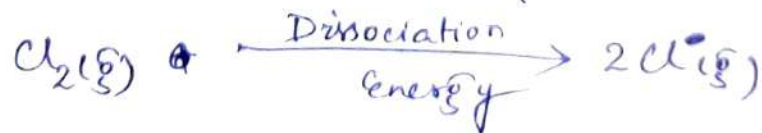
Measurement of Electron Affinity

\rightarrow Conversion of metallic sodium into gaseous Na atom.



S \rightarrow sublimation energy

\rightarrow Gaseous Cl_2 molecules to gaseous Cl atom



Question (1Q)

1. What is periodicity of element?
2. What are the O.S of p-block elements?

1Q

1. Write down the factors affecting ionisation energy?
2. What is meant by Slater's Rule?
3. Write down the different characteristics of Slater's Rule?
4. Calculate the effective nuclear charge for Mg and P.

Ans. 1. The recurrence of elements with similar properties after certain regular interval when these are arranged in the increasing order of their atomic numbers is called periodicity.

2.

Group No.	13	14	= 15	16	17	18
Highest O.S	+3	+4	+5	+6	+7	+8
Other observed O.S	+1	+2, -4	+3, -3	+4, +2, -2	+5, +3 +1, -1	+6, +4, +2

Long Questions

1. Factors influencing ionisation enthalpy.

(i) Size of the atom: As the distance between the electron and the nucleus increases, it becomes easier to remove an outermost electron. Thus ionisation enthalpy decreases with increase in atomic size.

(ii) Charge on the nucleus: Ionisation enthalpy increases with increase ~~not~~ in nuclear charge because of the increase in the attractive force b/w the nucleus and the e^- .

(iii) Screening effect of inner \bar{e} : Ionisation enthalpy decreases when the shielding effect of inner \bar{e} increases.

(iv) Penetration effect of electrons : The penetration power of the electrons in various orbitals decreases in a given shell in the order : $s > p > d > f$.

(v) Effect of half filled and completely filled sub-levels : The ionisation enthalpy is higher than that of expected.

2. The general principle behind Slater's Rule is that the actual charge felt by an \bar{e} is equal to what we did expect the charge to be from a certain no. of protons, but minus a certain amount of charge from other electrons.

~~Screening~~ Important

1. Why the 1st ionisation potential of an element is less than the 2nd ionisation potential?

2. Electron affinity :

Amount of energy released when an electron added to a gaseous isolated atom or ion.

3. Why the nitrogen has negative electron affinity?

4. Why the electron affinity of fluorine is less than chlorine.

Electron affinity of fluorine is unexpectedly low because small size of atom. The addition of an extra electron produces high electron charge density in a relatively compact 2p subshell resulting in strong electron-electron repulsion. The repulsive forces b/w \bar{e} release low electron affinity of fluorine than chlorine.

Imp
5. How the bond angle of hydrides of Group 16 elements varies with decreasing electro negativity of central atom beyond the group.

6. What are the main groups transition and inner transition element.
7. How are the transition element are distinguish from main group element from electronic configuration.
8. Would you call Zn and Hg as s block or d block element. Give reasons for your answer.

Ans

1. The 1st ionisation energy is less than the second ionisation energy because the electrons are tightly bound by the positive atom due to increased attraction force.
2. Nitrogen has negative electron affinity because its electronic configuration is $2s^2 2p^3$ i.e. has half filled p-orbital. That's why it doesnot accept more e^- as it has stable configuration.
5. The bond angle of hydrides of grp 16 decreases down the group with decreasing electronegativity of central atom because the lone pair - bond pair repulsion is stronger than the lone pair - lone pair or bond pair, bond pair interaction. ~~But at the electro~~
6. Main Group transition ~~metal~~ element include active metals of group 1, 2 and 13 to 18.
- Inner transition element include 3 to 12 group.
7. Transition metals are the only group of elements whose valence electrons are found in more than one shell, or energy level. This allows for many O.S. Other groups of elements only have valence e^- in the outermost electron shell.
8. Zn, Hg are s-block elements because they exhibit completely filled orbitals in their ground states and in their general O.S. as well.

Metallic Radii (or Covalent Radii of Metallic Atoms)

→ Most of the metals don't form covalent compounds. Metallic hydrides and organometallic compounds are, however, exceptions.

$$\text{Atomic volume of metallic phase} = \frac{\text{Atomic mass of metal atom}}{\text{Density of metal atom}}$$

Metallic Radii: It is defined as "Half of the inter-nuclear distance between two adjacent atoms in a metallic bond."

* Metallic radius is larger than covalent radius. The reason is that there is no actual overlapping of atomic orbitals in metallic bond. There is, however, overlapping of orbitals in covalent bonds.

Ex. Metallic radius of Na = 1.86 \AA
Covalent radius of Na = 1.54 \AA

Tetrahedral And Octahedral Radii

Tetrahedral Radii: This type of covalent radius is present in crystals with the diamond, sphalerite (zinc blende) and wurtzite arrangements. In such arrangements, each atom is surrounded by four other atoms (same or different atoms) tetrahedrally.

Octahedral covalent Radii: This type of structure is present in crystals with the pyrite (FeS_2) structure or a closely related structure of arsenopyrite (or marcasite) type.

Trends in Periodic Property of s and p-block

As we move from left to right in a period, the atomic no. i.e. nuclear charge goes on increasing. The electrons get added in the same shell. The added electrons do not screen the nucleus appreciably. The attraction of the nucleus for the outermost electrons goes on increasing. As a result:

- (i) Atomic radius (or effective covalent radius) goes on decreasing.
- (ii) Cationic radius as well as anionic radius goes on decreasing.
- (iii) Though atomic radii decrease along a period but at the end of each period, there is increase in the atomic radii of noble gases. It is because in case of noble gases the atomic radii are van der Waal radii.

→ As we move down the group in the periodic table, the atomic no. i.e. nuclear charge goes on increasing.

Electronegativity: The tendency or power of an element in a molecule to attract the shared pair of electrons towards itself is known as its electronegativity.

Trend in electronegativity:

- (i) As we move along a period in the periodic table, the nuclear charge goes on increasing. The e^- are added in same shell. These electrons hence do not screen the nucleus appreciably. The force of attraction of the valence electron goes on increasing.

As a result: the effective nuclear charge $>$ screening effect.

- (ii) As we go down a group, nuclear charge increases, e^- s are added to new shell, so force of attraction decreases. The force of attraction of the nucleus goes on decreasing.

As a result: the effective nuclear charge $<$ screening effect.