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Periodic Classification of Elements

Mendeleev's Old Periodic Law

According to this law, "The physical and chemical properties of the elements are the periodic function of their atomic masses."

i.e. if different elements are arranged in increasing order of their atomic masses, after certain regular intervals the elements having similar properties are repeated.

Mendeleev's Modern Periodic Law

On experimental basis, Mossley found that atomic number is the fundamental property of the elements but not atomic mass. Based on this fact he modified Mendeleev's Old Periodic Law and gave Mendeleev's Modern Periodic Law. According to this law,

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

Thus, if different elements are arranged in increasing order of their atomic numbers, after certain regular intervals (2,8,18,32,-----) the elements having similar properties are repeated. This is called periodicity of properties.

Long Form of Periodic Table

It has been found that, the properties of elements depend upon their electronic configuration and especially upon their outer shell electronic configuration. The elements having similar outer shell electronic configuration have similar properties while those having different outer shell electronic configuration have different properties.

Long form of periodic table, gives a correlation between the electronic configuration of element and its position in periodic table. It was for the first time prepared by Rang, Werner and Bury. It is based upon Bohr's scheme of electronic configuration. Hence, it is also called Bohr's Periodic Table.

The important characteristics of Long form of periodic table are as under-

(1) It is based upon electronic configuration of elements and gives a correlation between the electronic configuration of element and its position in periodic table.

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(2) In this periodic table, there are in all seven horizontal rows of elements called Periods (I to VII) and in all eighteen vertical columns called Groups (1 to 18).
(3)) I^{st} period contains only 2 elements and is called very short period. II^{nd} and III^{rd} periods contain 8 elements each and are called Short periods. IV^{th} and V^{th} periods contain 18 elements each and are called Long periods. VI^{th} period containing 32 elements Longest period of periodic table. VII^{th} period is incomplete period of periodic table.
(4) In elements of group 1 and 2 only outer most shell is incompletely filled and last electron enters in s-orbital of outer most shell. These elements are called s-block elements. The general outer shell electronic configuration of these elements is ns^{1-2}.
(5) In elements of group 13 and 18 only outer most shell is incompletely filled and last electron enters in p-orbitals of outer most shell. These elements are called p-block elements. The general outer shell electronic configuration of these elements is ns^2np^{1-6}.
(6) In elements of group 3 and 12 outer two shells are incompletely filled and last electron enters in d-orbital of penultimate shell i.e. (n-1)d-orbitals . These elements are called d-block elements. The general outer shell electronic configuration of these elements is ns^2,$(n-1)d^{1-10}$.

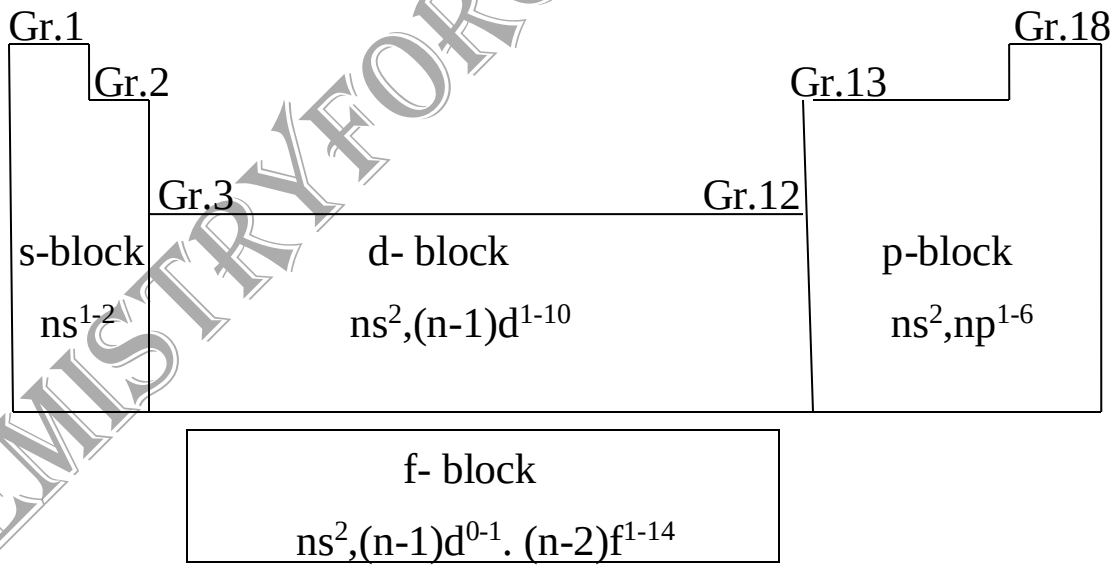


Fig.- Long Form of Periodic Table

(7) There are two series of 14 elements each (4f and 5f series) below the periodic table. In these elements outer three shells are incompletely filled and last electron

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enters in f-orbitals of anti-penultimate shell i.e. (n-2)f-orbitals . These elements are called f-block elements. The general outer shell electronic configuration of these elements is ns^2,$(n-1)d^{0-1}$. $(n-2)f^{1-14}$.

s and p-block elements where only outer most shell is incompletely filled are collectively called **Representative Elements**.

d-block elements where outer two shells are incompletely filled show transition in properties between highly electropositive s-block elements and highly electronegative p-block elements. Hence, these elements are collectively called **Transition Elements**.

f-block elements where outer three shells are incompletely filled lie between transition elements. Hence, these elements are collectively called **Inner Transition Elements**.

If a diagonal is drawn from Boron to Astatine then it roughly devides metals and non-metals. All the elements (except H) lying left hand side of this diagonal are metals while those lying right hand side are non-metals. The elements lying near this diagonal (Ge, As, Sb & Te) are Metalloids. The elements lying on this diagonal (B, Si & At) are also non-metals.

Cause of periodicity of properties

It has been found that, the properties of the elements depend upon their electronic configuration and especially upon their outer shell electronic configuration. The elements having similar outer shell electronic configuration have similar properties while those having different outer shell electronic configuration have different properties. When different elements are arranged in increasing order of their atomic numbers, after certain regular intervals (2,8,18,32,-----) the elements having similar outer shell electronic configuration are repeated and therefore, the properties are repeated. Thus, **the repetition of similar outer shell electronic configuration after certain regular intervals is the principal cause of the periodicity of properties in periodic table.**

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Periodic Properties

Those properties which are repeated periodically in periodic table are called periodic properties.

Most common periodic properties are as under-

(1) Valency
(2) Atomic size
(3) Ionic size
(4) Ionization enthalpy
(5) Electron gain enthalpy
(6) Electronegativity

(1) Atomic radius or atomic size

The distance from the centre of the nucleus of an atom to its last electron is called atomic radius of the atom.

The atomic radius is the measure of atomic size. The greater the value of atomic radius, larger is the atomic size.

Atomic radius of an element depends upon following factors -

(i) Nature of element
(ii) Number of shells between nucleus and valence shell
(iii) Nature of bond
(iv) Bond multiplicity
(v) Nature of neighbouring atoms

According to Heisenberg's uncertainty principle, the position of the outermost electron cannot be determined accurately. Hence, the atomic radius of an atom cannot be determined accurately. In fact, the atom of the same element have different atomic radius in different conditions.

Depending upon the nature of bond formed by the atom, atomic radius may be of following types-

(a) Covalent Radius

"One -half of the inter-nuclear distance of two bonded atoms in a homo-nuclear diatomic covalent molecule is called covalent radius of the atom."

Mathematically,

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$$\textbf{Covalent radius} = \frac{Inter-nuclear\ distance}{2}$$

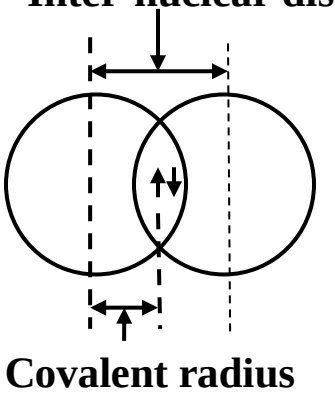


Fig.- Covalent radius for Cl atoms in homo-atomic Cl_2 molecule

For example, for Cl_2 molecule, inter-nuclear distance = 1.99 A^0
Hence, Covalent radius of chlorine atom = 1.99/2
= 0.99 A^0

For, hetero-nuclear diatomic molecule, covalent radius is defined as under-

"The distance from the centre of the nucleus of an atom to the shared electron pair is called covalent radius of the respective atom."

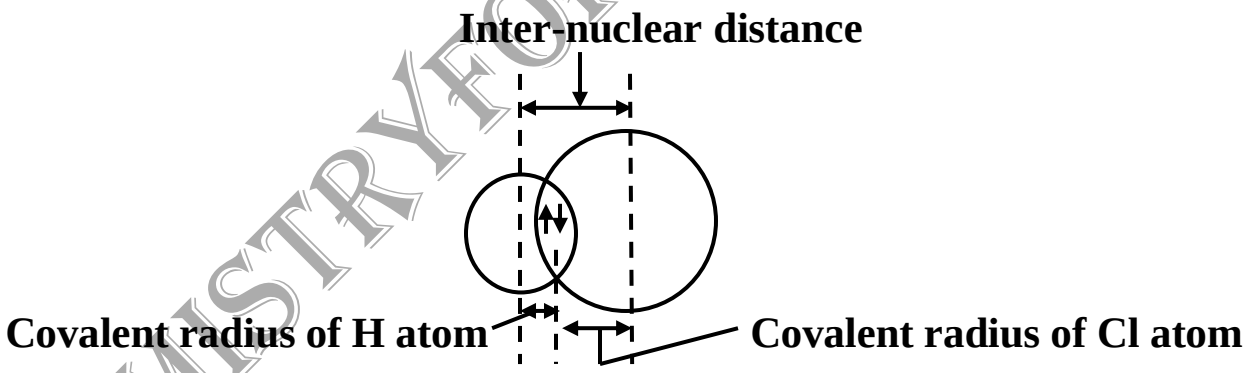


Fig.- Covalent radii of H and Cl atoms in hetero-atomic HCl molecule

Here, Inter-nuclear distance can be determined by electron diffraction method. Hence, if covalent radius of one atom is known, that of other atom can be calculated.

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(b) Metallic Radius or Crystal Radius

In metallic crystals, same sized metal atoms remain arranged touching each other. Here,

"One -half of the inter-nuclear distance of two nearest atoms of a metallic crystal is called metallic radius or crystal radius of the metal."

Mathematically,

$$\textbf{Metallic radius} = \frac{Inter-nuclear\ distance\ of\ two\ nearest\ atoms}{2}$$

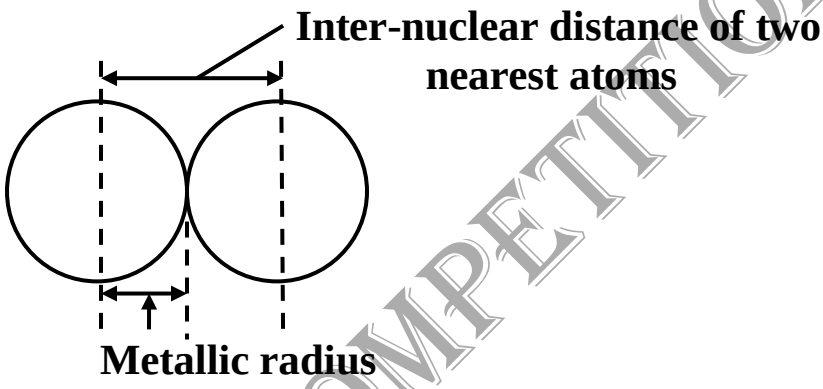


Fig.- Metallic radius of a metal

For example, for sodium, inter-nuclear distance of two nearest atoms

$= 3.72\ A^0$

Hence, Metallic radius of sodium $= 3.72/2$

$= 1.86\ A^0$

Here, Inter-nuclear distance can be determined by X-ray diffraction or electron diffraction method

(c) van der Waal Radius

"One -half of the inter-nuclear distance of two nearest atoms belonging to two nearest molecule in solid state of a covalent substance is called vander waal radius of the atom."

Mathematically,

$$\textbf{van der Wall radius} = \frac{Inter-nuclear\ distance\ of\ two\ nearest\ atoms\ belonging\ to\ two\ nearest\ molecules}{2}$$

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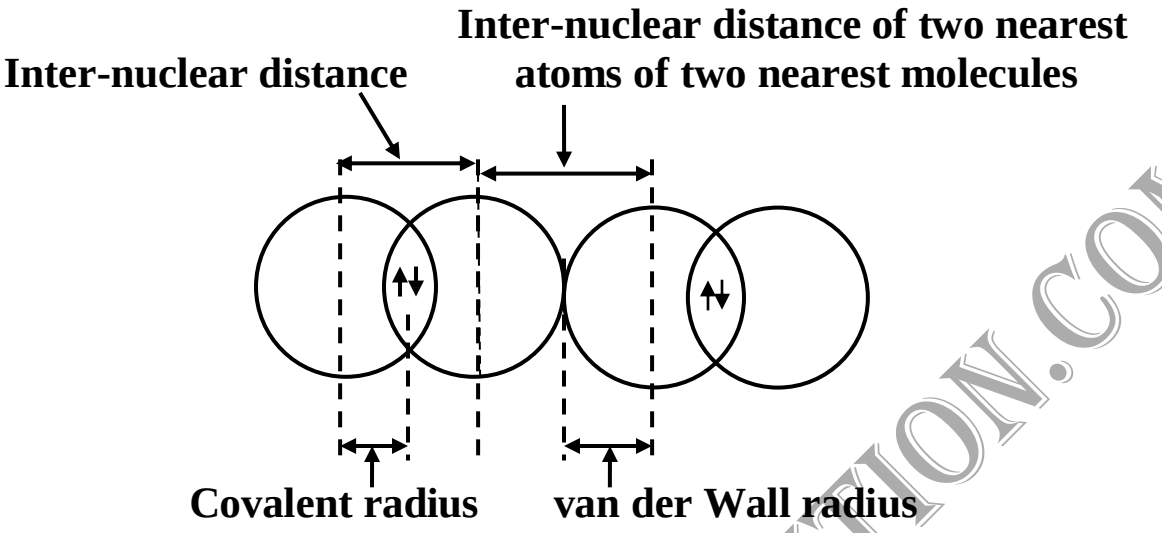


Fig.- Expression of van der Waal radius

For example, for Cl_2 molecule, inter-nuclear distance of two nearest atoms of two nearest molecule in solid state = 3.60 A^0

Hence, vander Waal radius of chlorine atom = 3.60/2

= 1.80 A^0

Periodicity of Atomic radius

On moving left to right in a period of periodic table, atomic radius goes on decreasing continuously from alkalies metals (Gr. 1) to halogens (Gr. 17), but zero group elements (Gr. 18) exceptionally have biggest atomic radius in a period, even bigger than alkalies metals due to their closed octet electronic configurations.

In fact, on moving left to right in a period, nuclear charge increases, but electrons enter in same shell. Hence, nuclear attraction on valence electrons increase so that the electrons are more strongly pulled towards the nucleus. Thus, atomic radius decreases across the period. Here, amongst reactive elements alkalies metals have biggest atomic radius while halogens have the smallest atomic radius in a period.

Atomic Radius decreases →

Atomic Radius Increases ↓								
	Li	Be	B	C	N	O	F	Ne
	Na	Mg	Al	Si	P	S	Cl	Ar
	K	Ca						

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On moving top to bottom in a group, atomic radius goes on increasing as new shells are added one by one.

- Order of covalent, metallic and vander Waal radii for a definite element-

$$r_{\text{vander Waal}} > r_{\text{metallic}} > r_{\text{covalent}}$$

- **vander Waal Force** – It is one of the weakest physical force of nature which operates amongst non-bonded atoms and molecule. It arises due to-
  (1) Dipole- Dipole Interaction
  (2) Dipole- Induced Dipole Interaction
  (3) Induced Dipole- Induced Dipole Interaction

(2) Ionic Radius

In ionic crystals, oppositely charged ions remain arranged alternatively. Here, "The distance from the centre of nucleus of an ion to the point where its effective electron density ceases is called ionic radius of the respective ion."

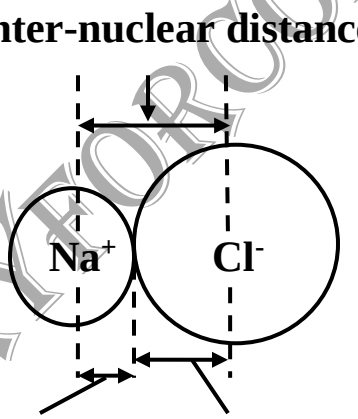


Fig.- Ionic radius of Na^+ and Cl^- ions

Here, the sum of ionic radii of cation and anion corresponds to the inter-nuclear distance of the two nearest ions. The value of inter-nuclear distance can be determined using X-ray diffraction method. Thus, if ionic radius of one of the ions is known, that of other ion can be calculated.

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It has been found that-

(1) Ionic radius of cation is always smaller than that of original atom.

(2) Ionic radius of anion is always bigger than that of original atom.

Q. Give the reason - Ionic radius of cation is always smaller than that of original atom.

Ans.- Cations are formed by removal of one or more electrons from the neutral atoms.

$$M \rightarrow M^{n+} + ne^-$$

$$Na \rightarrow Na^+ + e^-$$

$$Mg \rightarrow Mg^{2+} + 2e^-$$

In general, during formation of cations all the electrons of the outermost shell are removed. Hence, outermost shell gets vanished and the size of cation becomes smaller than that of original atom.

Furthermore, after removal of one or more electrons the value of effective nuclear charge (Z_{eff}) i.e. average number of protons attracting each electron gets increased. Hence, electrons are more strongly attracted towards the nucleus. It results in the decrease in size of the cation.

Q. Give the reason - Ionic radius of anion is always bigger than that of original atom.

Ans.- Anions are formed by gaining of one or more electrons by the neutral atoms.

$$X + ne^- \rightarrow X^{n-}$$

$$F + e^- \rightarrow F^-$$

$$O + 2e^- \rightarrow O^{2-}$$

After gaining of one or more electrons, the value of effective nuclear charge (Z_{eff}) i.e. average number of protons attracting each electron gets decreased. Hence, electrons are less strongly attracted towards the nucleus. It results in the increase in size of the anion.

Iso-electronic ions

The ions containing same number of electrons are called iso-electronic ions. The ionic radius of iso-electronic ions goes on decreasing on moving left to right in a period of periodic table. For example, the order of ionic radii of some important iso-electronic ions is as under-

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$$Na^{+} > Mg^{2+} > Al^{3+}$$
$$N^{3-} > O^{2-} > F^{-}$$

In fact, on moving left to right in a period of periodic table, the value of effective nuclear charge (Z_{eff}) i.e. average number of protons attracting each electron gets increased. Hence, electrons are more strongly attracted towards the nucleus. It results in the decrease in size of the ion.

Periodicity of Ionic radius

On moving left to right in a period of periodic table, ionic radius of iso-electronic ions decreases because of the increase of effective nuclear (Z_{eff}) i.e. average number of protons attracting each electron.

On moving top to bottom in a group, ionic radius goes on increasing as number of shells in the ion goes on increasing.

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