

Unit: 3 Classification of Elements & Periodicity

⇒ Periodic classification of Elements?

A classification in which elements are arranged in the order of increasing atomic weights/atomic numbers in the manner that the elements with similar properties appear at regular intervals, is called periodic classification of elements.

Lavoisier first of all classified elements into metals & non-metals, but this was rather vague. The first significant and systematic classification of elements was given by Mendeleev (1869) in the form of periodic table, commonly known as Mendeleev's periodic table. This is based on atomic mass & also a periodic law given by studies of physical & chemical properties of elements. Present/Modern periodic classification is based on atomic number/electronic conf. which we have discussed here.

⇒ Modern Periodic classification/s, p, d & f-classification of Elements:

After discovery of electronic configuration by Bohr, Mosley periodic law has been modified, which is known as Modern periodic law. It states as - "Physical & Chemical properties of elements are periodic function of their electronic confs."

When elements are arranged in order of their increasing atomic numbers, i.e.; Electronic conf. and found a periodicity in their properties, a tabular arrangement of the elements is obtained which is known as Modern periodic table.

Modern periodic table/classification, which is based on atomic nos, i.e.; electronic configuration divide elements in four types/blocks - s, p, d & f depending upon the nature of the atomic orbital into which last/differentiating electron enters. Such classification of elements is called s, p, d & f classification.

1. s-block elements: Elements in which last or differentiating electron enter in outermost (ns) orbital are called s-block elements. They have outer ele. conf. ns^1 or ns^2 i.e., $ns^{1 \text{ or } 2}$ ($n=1$ to 7). They are elements of Group 1 & 2, and situated at extreme left position in the periodic table. Total number of s-block elements is 13.

Group-1: (H), Li, Na, K, Rb, Cs, Fr (Alkali metals); H is non-metal & gas.

Group-2: Be, Mg, Ca, Sr, Ba, Ra (Alkaline earth metals)

Characteristics: (i) They are strong electropositive solid elements/metals (except H).

(ii) They show constant valency/oxidation state +1 (Gr. 1) / +2 (Gr. 2).

(iii) They show constant valency/oxidation state +1 (Gr. 1) / +2 (Gr. 2).

(iv) They have large atomic/ionic radii and low ionisation enthalpy & energy.

(v) They are soft, malleable and good conductor of heat & electricity.

(vi) Their compounds/ions are colourless/white, and diamagnetic property.

(vii) They generally impart colouration to the flame (except Be, Mg).

(viii) They act as good reducing agents. (viii) They generally form ionic compds.

(ix) They are highly reactive with O_2 , H_2O , non-metals etc.

(x) Their oxides, hydroxides, carbonates, bicarbonates are strong basic.

2. p-block elements: Elements in which last or differentiating electrons enter in outer most p-orbital (np) are called p-block elements. They have outer electronic conf. $ns^2 np^{1-6}$. They include elements of Group 13 to 18 (metals, non-metals & metalloids). They are situated

at extreme right position in the periodic table. (2)

Group-13 (ns^2np^1): B, Al, Ga, In, Tl, Nh (Boron group)

Group-14 (ns^2np^2): C, Si, Ge, Sn, Pb, Fl (Carbon group)

Group-15 (ns^2np^3): N, P, As, Sb, Bi, Mc (Nitrogen group)

Group-16 (ns^2np^4): O, S, Se, Te, Po, Lv (Oxygen group)

Group-17 (ns^2np^5): F, Cl, Br, I, At, Ts (Halogens group)

Group-18 (ns^2np^6): He, Ne, Ar, Kr, Xe, Rn, Og (Noble gases)

Total number of elements of p-block is $3 \times 6 + 1$ (He, which has $1s^2$ conf., but placed in Gr. 18 (p-block) due to similarity properties with them. maybe s-block element)

* Elements of s & p-blocks (except Gr. 18) are collectively called normal/representative/non-transition elements. * Elements of periods 2 & 3 are called typical elements.

Characteristics: (i) They are generally electronegative elements, i.e., non-metals. However, some

(Al, Ga, In, Tl, Sn, Pb, Bi...) are metals and some (Si, Ge, As, Sb, Te, Po, At) are metalloids.

(ii) They may be solids, liquids or gases.

(iii) They (except C, metals) are bad conductor of heat & electricity. C & metals are good conductor of heat & electricity.

(iv) They generally show variable valencies/oxidation states.

(v) They generally have high ionisation energy and low oxidation potentials, so they are more oxidising/less reducing property.

(vi) They usually form covalent compounds, although ionic character increases down a group.

(vii) Their compounds/ions are coloured as well as colourless, and diamagnetic.

(viii) Some (non-metals) of oxides/hydroxides are acidic and some (metals) oxides are amphoteric.

3. d-block elements: Elements in which last or differentiating electron enters in penultimate (i.e., $n-1$) d-orbitals are called d-block elements. They are also called transition metals, since their properties are intermediate of s- & p-block elements, and placed in between s- & p-blocks, i.e., middle position of P.T. Their outer electronic conf. is $(n-1)d^{1-10}ns^{0,1+2}$ ($n=4$ to 7). They include elements of Groups 3 to 10 in the form of 4 series as given below:

(i) 1st transition or 3d series: Sc_{21} to $Zn_{30} = 10$ elements ($3d^1 4s^2$ to $3d^{10} 4s^2$ conf.)

(ii) 2nd " 4d " : Y_{39} to $Cd_{48} = 10$ elements ($4d^1 5s^2$ to $4d^{10} 5s^2$ conf.)

(iii) 3rd " 5d " : La_{57} , Hf_{72} to Hg_{80} " ($5d^1 6s^2$ to $5d^{10} 6s^2$ conf.)

(iv) 4th " 6d " : Ac_{89} , Rf_{104} to Cn_{112} " ($6d^1 7s^2$ to $6d^{10} 7s^2$ conf.)

Total number of elements in d-block is 40.

Characteristics: (i) They are electropositive solid metals of high melting & boiling points (except Hg)

* (ii) They show variable valencies/oxidation states due to presence of incomplete d-orbitals which participate in valency/bonding in addition to ns-electrons.

(iii) They are generally malleable and ductile, due to relatively low ionisation energy (IE), few valency electrons (1 or 2) and a number of vacant orbitals.

(iv) They are good conductor of heat and electricity.

* (v) They and their compounds/ions are generally paramagnetic due to presence of one or more unpaired electron(s). However, Fe, Co, Ni are ferromagnetic.

* (vi) Their compounds/ions are generally coloured, due to d-d transition or charge transfer.

* (vii) They have tendency to form stable complex compounds, due to smaller size, higher nuclear charge, i.e., high (+ve) charge density and presence of vacant d-orbitals.

(viii) They have catalytic property, i.e., they or their compounds behave as catalyst in chemical reactions.

4. f-block elements: Elements in which last electron enters in antepenultimate i.e; $(n-2)$ f-orbitals are called f-block elements. Their outer electronic conf. are $(n-2) f^{1-14} (n-1) d^{0 \text{ or } 1} ns^2$ ($n=6$ or 7). They are members of Group 3, and of two series:

(a) 4f or 1st inner transition series: Ce_{58} to Lu_{71} ($4f$ orbitals gradually filled) ^{Elements in which}
 $(4f^1 5d^1 6s^2)$ $(4f^{14} 5d^1 6s^2)$

They are known as lanthanides/lanthanones, since they follow lanthanum (La_{57}). They are also called rare earth elements, as they found in trace amount in the earth crust.

(b) 5f or 2nd inner transition series: Elements in which 5f-orbitals gradually filled.

Th_{90} , Pa_{91} , U_{92} , Np_{93} to Lr_{103} . These are called actinides or actinones since they follow Actinium (Ac_{89}). First three elements (Th, Pa, U) are natural radioactive elements while rest (Np_{93} to Lr_{103}) are artificial radioactive elements, called trans-uranic elements, since follow Uranium (U_{92}).

f-block elements are collectively called inner transition elements. They are situated below main part of PT in two rows, each contains 14 elements.

Characteristics: (i) They are generally solid heavy metals/electropositive elements.

(ii) They show variable valencies/oxidation states. Common o. state is +3.

(iii) They and their compounds/ions are generally paramagnetic.

(iv) Their compounds/ions are generally coloured. Colours are due to f-f transition.

(v) They have tendency to form complex compounds of higher stability.

(vi) They show Lanthanide contraction (i.e; steady decrease in atomic/zionic radii with the increase of atomic numbers).

⇒ Atomic properties & Periodicity:

Properties of elements/atoms which vary atom to atom, and show gradation i.e, regular change in groups & periods of PT are called atomic properties. They are atomic/zionic radius, ionisation energy, electronegativity, electron affinity etc.

The repetition of the similar properties of elements placed in a group/period and appear after regular/definite intervals of atomic numbers is called periodicity. The cause of periodicity is recurrence/appearance of similar electronic configuration after regular intervals (2, 8, 18, 32-).

⇒ 1. Atomic radius:

The term atomic radius is generally used for the distance between the centre of the nucleus and the outer most orbit of electrons. According to quantum mechanics, there is no certainty with regard to the exact position occupied by electron at any point/time, and also it is impossible to isolate an individual atom. In spite of above limitations we need to have some operational definition of the term atomic radius as given below:

(a) Covalent radius (b) Vanderwaal radius (c) Metallic radius.

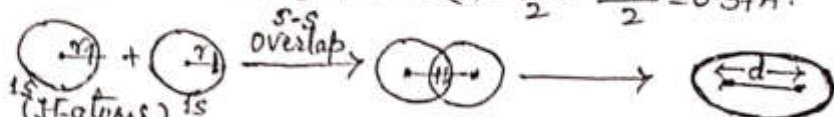
(a) Covalent radius: This is defined for those elements which can form covalent homo molecules, e.g. H_2, N_2, O_2, Cl_2 etc.



It is defined as "One half of the distance between the nuclei of two like atoms bonded together by a single covalent bond is called covalent radius".

This is determined by infrared spectroscopy and expressed in Å. For example, distance between two nuclei of H atoms (d) for H_2 molecule is 0.74 \AA .

$$\therefore \text{Covalent radius of H atom } (r) = \frac{d}{2} = \frac{0.74}{2} = 0.37 \text{ \AA}$$



(b) Vanderwaal radius: This is defined for those elements which may or may not form covalent bonds/molecules, e.g. He, Ne, H, Cl etc.

It is defined as "One half of the distance between nuclei of two neighbouring atoms or covalent molecules of the same substance held by Vanderwaal attraction is called Vanderwaal radius".

It is also determined by infrared spectro-

scopy and expressed in Å. For example, distance between two nuclei of closely/neighbouring H_2 molecules (d') is 2.4 \AA .

$$\therefore \text{Vanderwaal radius of H } (r') = \frac{d'}{2} = \frac{2.4}{2} = 1.2 \text{ \AA}$$

* By above discussion/figure, it is evident $\text{Vanderwaal radius } (r') > \text{Covalent radius } (r)$

(c) Metallic radius: It is defined for metals as "One half of the distance between nuclei of two adjacent atoms in the metallic lattice/crystal is called metallic radius".

It is determined by Bragg's X-ray diffraction method and expressed in Å.

For example, distance between nuclei of two adjacent Li atoms in metal crystal (d) is 3.04 \AA . \therefore Metallic radius of Li atom (r) = $\frac{d}{2} = \frac{3.04}{2} = 1.52 \text{ \AA}$.

* $\text{Metallic radius} > \text{Covalent radius}$ (Since metallic bond is weaker than covalent bond, therefore internuclear distance between two atoms in metallic bond is more than that of covalent bond).

* Different forms of atomic radius are in the order: $\text{Vanderwaal radius} > \text{Metallic radius} > \text{Covalent radius}$.

* Atomic radius of an element is normally expressed as covalent radius as it is easily determined.

\Rightarrow Factors affecting Atomic radius: A number of factors, which influence atomic radius, are as follows:

(i) No. of orbits (n): Atomic radius increases (square times) with increase of number of orbit (n), i.e., $\text{Atomic radius } (r) \propto n^2$.

For example, atomic radius/size of K_{19} is larger than that of Na_{11} . Since K_{19} has four orbits while Na_{11} has three orbits. Na_{11} : 2, 8, 1 ($n=3$); K_{19} : 2, 8, 8, 1 ($n=4$).

(ii) Nuclear charge (Z): Atomic radius decreases with the increase of nuclear charge (Z) as nuclear attraction on electron cloud (orbit) increases. $r \propto 1/Z$

for example, atomic radius/size of sodium is larger than that of Mg. This is because though Na & Mg have same no. of orbits but Mg has more nuclear charge (+12) than

Na(+11). So more nuclear attraction on electron cloud in former case, resulting contraction in size/atomic radius.

(iii) Screening/shielding effect: Decrease in the force of attraction exerted by the nucleus on the outermost electron due to the presence of electrons in the inner orbits/orbitals is called screening/shielding effect.

Order of shielding effect ^{different} orbitals: $s > p > d > f$

Effective nuclear charge (Z^*) = Total nuclear charge (Z) - Screening effect (σ), where Z = atomic number of an element. Atomic radius is directly proportional to effective nuclear charge, i.e.; Atomic radius increases with the increase of Z^* (Effective nuclear charge). Effective nuclear charge may also be expressed as Z/e .

Ques → For example, radius/size of Mg^+ is smaller than ^{that of} Mg . This is because effective nuclear charge of former (Mg^+) is more than that of Mg . Mg^+ : 2, 8, 1, $n=3$, $Z=+12$, $e=1$; Mg : 2, 8, 2, $n=3$, $Z=+12$, $e=12$. Z/e (Effective nuclear charge) for Mg^+ ($= \frac{12}{1} = 12$) $>$ Mg ($\frac{12}{12} = 1$).

⇒ Periodicity: Atomic radius vary along ^a period and down a group in P.T.

In group, atomic radius increases with the increase of atomic nos. down a group due to increase of number of orbits (n). e.g.; Gr. 1 $H < Li < Na < K < Rb < Cs < Fr$ (increasing order of atomic radius).

In period, atomic radius generally decrease from left to right direction due to increase of nuclear charge and hence nuclear attraction on outermost electron cloud/orbit. e.g., In 2nd period order of atomic radius: $Li > Be > B > C > N > O > F > Ne$.

⇒ Ionic radius: It defined as "the distance between the nucleus of an ion and the point to which the nucleus has influence on its electron cloud is called ionic radius". In practice, radius of an ion is difference of interionic distance and radius of other ion (anion). Ionic radius is known by determining interionic distance (d) in the ionic crystal by Bragg's X-ray diffraction method.

i.e., Radius of cation (r_c or r_+) + Radius of anion (r_a or r_-) = Interionic distance (d).

or, r_c or $r_+ = d - r_a$ or r_- for example, in $NaCl$, interionic distance (d) is 2.76 \AA & radius of Cl^- is 1.81 \AA , So radius of Na^+ (r_{Na^+}) = $2.76 - 1.81$

* The radius of cation (r_+) is smaller than that of neutral atom (atomic radius = 0.95 \AA) due to increase of effective nuclear charge (Z/e or Z^*) so contraction in size occurs.

Ques → For example, ^{radius} size of Na^+ is less than that of Na (i.e., $r_{Na^+} < r_{Na}$). This is because effective nuclear charge in Na^+ is more ($\frac{11}{10} = 1.1$) than Na ($\frac{11}{11} = 1$) so, more nuclear attraction on outermost electron cloud/orbit in former case than latter resulting contraction in size, i.e.; decrease of atomic/ionic radius.

* The radius of anion (r_-) is larger than that of neutral atom/atomic radius, due to decrease of effective nuclear charge, so expansion in size occurs.

Ques → For example, Radius or size of Cl^- is larger than that of Cl , i.e.; $r_{Cl^-} > r_{Cl}$. This is because effective nuclear charge in Cl^- is less ($\frac{17}{18} = 0.94$) than Cl ($\frac{17}{17} = 1$). So, less nuclear attraction on outermost electron cloud/orbit in case of Cl^- resulting expansion in size, i.e.; increase of atomic/ionic radius.

Thus Order of radii of Cation, Anion & Neutral atom: $r_{M^+} < r_M < r_{M^-}$.

* Factors affecting & Periodicity of ionic radius are similar as atomic radius.