PERIODICITY

(a) The regular gradation in properties from top to bottom in a group and from left to right in a period is called periodicity in properties.

(b) In a period, the ultimate orbit remain same, but the number of e^- gradually increases.

(c) In a group, the number of e^- in the ultimate orbit remains same, but the values of n increases.

Causes of periodicity

(a) The cause of periodicity in properties is due to the same outermost shell electronic configuration coming at regular intervals.

(b) In the periodic table, elements with similar properties occur at intervals of 2, 8, 8, 18, 18 and 32. These numbers are called as magic numbers.

Periodic Properties

Valency : It is defined as the combining capacity of the elements. The word valency is derived from an Italian word "Valentia" which means combining capacity.

Old concept : Given by : **Frankland**

Valency with respect to Hydrogen : Valency of H = 1

It is defined as the number of hydrogen atoms attached with a particular element.

	IA	IIA	IIIA	IVA	VA	VIA	VIIA
	NaH	MgH_2	AlH_3	SiH_4	PH_3	H_2S	H–Cl
Valency	1	2	3	4	3	2	1

Note : Valency w.r.t. H across the period increases upto 4 and then again decreases to 1.

Valency with respect to oxygen : Valency of 'O' = 2

It is defined as twice the number of oxygen atoms attached with a particular atom.

	IA	IIA	IIIA	IVA	VA	VIA	VIIA
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
Valency	1	2	3	4	5	6	7

Note : Valency with respect to oxygen increases from 1 to 7 across the period. Valency w.r.t. 'O' is equal to the group number.

New concept : This concept is based on the electronic configuration. According to this concept valency for IA to IVA group elements is equal to number of valence shell e^- and from VA to zero group, it is – [8– (number of valence e^-)].

	Valency = No. of valence e				Valency = (8– no. of valence e^-)			
	IA	IIA	IIIA	IVA	VA	VIA	VII	0
	ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
Valence shell e	1	2	3	4	5	6	7	8
Valency	1	2	3	4	3	2	1	0
					(8 – 5) = 3			(8 – 8) = 0

Note : All the elements of a group have same valencies because they have same number of valence shell electrons.

SCREENING EFFECT (σ) AND EFFECTIVE NUCLEAR CHARGE (Z_{eff})

(a) Valence shell e^- suffer force of attraction due to nucleus and force of repulsion due to inner shell electrons.

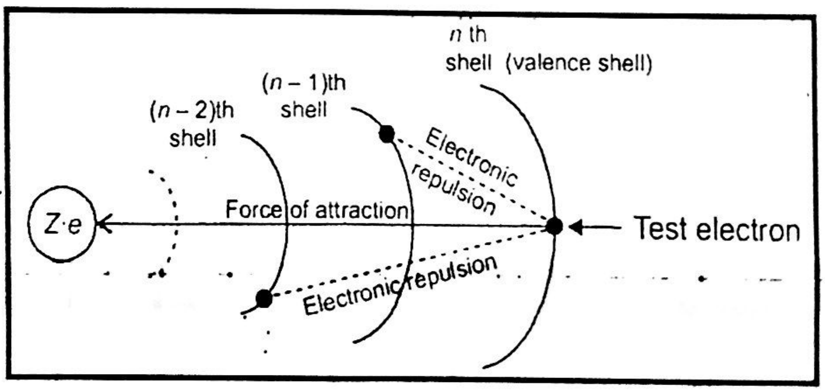
(b) The decrease in force of attraction on valence e^- due to inner shell e^- is called screening effect or shielding effect.(i.e. total repulsive force is called shielding effect.)

(c) Due to screening effect. valence shell e^- experiences less force of attraction exerted by nucleus.(i.e. total attraction force experienced by valence e^- is called Zeff.)

(d) There is a reduction in nuclear charge due to screening effect. Reduced nuclear charge is called effective nuclear charge.

(e) If nuclear charge = Z, then effective nuclear charge = Z – σ (Where σ (Sigma)= Screening constant)

So, Zeff = (Z – σ)



Slater's rule to know screening constant (σ) :

(a) Screening effect (S.E.) of one e^- of the 1s is 0.30. Ex He ($1s^2$)

Screening effect of one 1s e^-. where σ = 0.30

$\therefore$ Zeff = Z – σ = 2 – 0.30 = 1.7

(b) Screening effect of ns and np (outermost orbit) electron is 0.35

(c) Screening effect of (n – 1) penultimate orbit s, p, d electrons is 0.85

(d) Screening effect of (n – 2) and below all the e^- present in s, p, d, f is 1.0

(c) Screening effect of (n − 1) penultimate orbit s, p, d electrons = 0.85

(d) Screening effect of (n − 2) and below ... [illegible] = 1.0

(Effective Nuclear charge of elements of second period)						
Element	Electronic Configaration	Z	σ of ns & np electron (a)	σ (n−1) orbital (b)	Total Screeing Constant (a + b)	Effective nuclear charge Z*=Z − σ
$_3$Li	$1s^2\ 2s^1$	3	–	0.85 2=1.70	1.70	1.30
$_4$Be	$1s^2,\ 2s^2$	4	1 0.35=0.35	0.85 2=1.70	2.05	1.95
$_5$B	$1s^2,2s^2,2p^1$	5	2 0.35=0.70	0.85 2=1.70	2.40	2.60
$_6$C	$1s^2,2s^2,2p^1$	6	3 0.35=1.05	0.85 2=1.70	2.75	3.25
$_7$N	$1s^2,2s^2,2p^3$	7	4 0.35=1.40	0.85 2=1.70	3.10	3.90
$_8$O	$1s^2,2s^2,2p^4$	8	5 0.35=1.75	0.85 2=1.70	3.45	4.55
$_9$F	$1s^2,2s^2,2p^5$	9	6 0.35=2.10	0.85 2=1.70	3.80	5.20

Periodic variation

(a) From left to right in a period Zeff increases

(i) That is why in a period Zeff increases by 0.65 and hence atomic size decreases considerably.

(ii) In transition series Z increase by + 1 but screening effect increases by 0.85 So Zeff is 0.15

(1− 0.85 = 0.15) [Because e^- enters in (n − 1) orbit which has value of σ = 0.85]

In transition series Zeff increases very less amount, by 0.15 from left to right and hence atomic size remains almost constant.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Zeff	3.00	3.15	3.30	3.45	3.60	3.75	3.90	4.05	3.70	4.35

(b) From top to bottom in a group Zeff remain constant

Element	Li	Na	K	Rb	Cs	Fr
Zeff	1.30	2.20	2.20	2.20	2.20	2.20

ATOMIC RADIUS

The average distance of valence shell e^- from nucleus is called atomic radius. It is very difficult to measure the atomic radius because –

(i) The isolation of single atom is very difficult.

(ii) There is no well defined boundary for the atom. (The probability of finding the e^- is 0 only at infinity).

So, the more accurate definition of atomic radius is –

Half the inter-nuclear distance(d) between two atoms in a homoatomic molecule is known as atomic radius.

This inter-nuclear distance is also known as bond length. Inter-nuclear distance depends upon the type of bond by which two atoms combine.

Based on the chemical bonds, atomic radius is divided into four categories –

1. Covalent radius 2. Ionic radius 3. Metallic radius 4. Vander waal radius

1. **Covalent radius**

One half of the distance between the nuclei (internuclear distance) of two covalently bonded atoms in homodiatomic molecule is called the covalent radius of that atom. The covalent bond must be single covalent bond. The covalent radius (r_A) of atom A in a molecule A_2 may be given as:

$$r_A = \frac{d_{A-A}}{2}$$

i.e. the distance between nuclei of two single covalently bonded atoms in a homodiatomic molecule is equal to the sum of covalent radii of both the atoms

$$d_{A-A} = r_A + r_A$$

In a heterodiatomic molecule AB where the electronegativity of atoms A and B are different, the experimental values of internuclear distance d_{A-B} is less than the theoretical values ($r_A + r_B$).

According to Schomaker and stevenson –

$$D_{A-B} = r_A + r_B - 0.09\ \Delta_x$$

Where Δ_x is the difference of electronegativities of the atoms A and B.

According to Pauling – If the electronegativities of the two atoms A and B are x_A and x_B respectively then

$$D_{A-B} = r_A + r_B - (C_1x_A - C_2x_B)$$

C_1 and C_2 are the Stevenson's coefficients for atoms A and B respectively.

2. **Metallic Radius**

Metal atoms are assumed to be closely packed spheres in the metallic crystal. These metal atom spheres are considered to touch one another in the crystal. One half of the internuclear distance between the two closest metal atoms in the metallic crystal is called metallic radius.

Metallic > Covalent radius

For example – Metallic radius and covalent radius of potassium are 2.3 Å and 2.03 Å respectively.

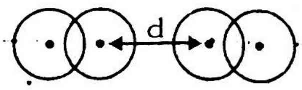
3. **Van Der Wall's Radius or Collision radius**

The molecules of non metal atoms are generally gases. On cooling, the gaseous state changes to solid state.

In the solid state, the non metallic elements usually exist as aggregations of molecules are held together by van der wall forces. **One half of the distance between the nuclei of two adjacent atoms belonging to two neighbouring molecules of a compound in the solid state is called van der walls radius.**

It may also be defined as half of the inter nuclear distance of two non bonded neighbouring atoms of two adjacent molecules.

2 . vander waal's radius



van der Wall's radius = $\frac{1}{2}$ Internuclear distance between two successive nuclei of two covalent molecules (d)

Van der wall's radius > Metallic radius > Covalent radius

The vander walls radius and covalent radius of chlorine atom are 1.80 Å and 0.99 Å respectively

4. **Ionic Radius**

A neutral atom changes to a cation by the loss of one or more electrons and to an anion by the gain of one or more electrons. The magnitude of charge on cation and anion is equal to the number of electrons lost or gained respectively. The ionic radii of the ions present in an ionic crystal may be calculated from the inter molecular distance between the two ions.

(a) **Radius of Cation**

Radius of cation is smaller than that of corresponding atom.

Reasons

(i) During the formation of cation either one shell is removed or

(ii) After removing an electron effective nuclear charge increase.

(b) **Radius of an Anion**

Radius of an anion is invariably bigger than that of the corresponding atom.

Reasons

(i) The effective nuclear charge decrease in the formation of anion. Thus the electrostatic force of attraction between the nucleus and the outer electrons decreases as the size of the anion increases.

(ii) Interelectronic repulsion increases.

Factors affecting atomic radius are

(a)	Atomic radius $\propto \dfrac{1}{\text{Effective nuclear charge (Zeff)}}$ Li > Be > B > C > N > O > F	(b)	Atomic radius ∝ number of shells Li < Na < K < Rb < Cs
(c)	Atomic radius ∝ Screening effect	(d)	Atomic size ∝ Magnitude of –ve charge $O < O^{-} < O^{-2}$
(e)	Atomic radius $\propto \dfrac{1}{\text{Magnitude of +ve charge}}$ $Mn > Mn^{+2} > Mn^{+3} > Mn^{+4}$	(f)	Atomic radius $\propto \dfrac{1}{\text{Bond order}}$ $>N-N<\ >\ -N=N-\ > N\equiv N$

Periodic variation of atomic radius

(a) **Across a period** : It decreases from left to right in a period as nuclear charge increases

Ex. Li > Be > B > C > N > O > F < Ne

(b) **In a group** : It increases from top to bottom in a group as number of shell increases

Ex. Li < Na < K < Rb < Cs

Exceptions

(a) **Transition elements**

Sc Ti V Cr Mn — Z_{eff} > Screening effect

Fe Co Ni — Z_{eff} ≈ Screening effect

(b) **Lanthanide Contraction**

(i) Outermost electronic configuration of inner transition elements is

$(n-2)\ f^{1-14},\ (n-1)s^2p^6d^{0-1},\ ns^2\ (n = 6 \text{ or } 7)$

(ii) e^- enters in $(n-2)$ f orbitals

(iii) Mutual screening effect of e^- is very less, because of complicated structure of f-orbital

(iv) Nuclear charge increases by one (+1) in lanthanides and actinides so atomic size of these elements slightly decreases. It is known as lanthanide contraction. Its effect is also observe in 5d transition series.

Here Nuclear charge > Screening effect.

(v) In 1st, 2nd and 3rd transition series, Radii – 3d < 4d ≈ 5d (except IIIrd B)

	IIIB	IVB	
size	Sc	Ti ↓	size increases
increases	Y	Zr	} Equal due to lanthanide contraction
	La	Hf	

(c) **Transition contraction :**

IIIA → B<Al ≈ Ga   Note : While atomic size should increases down the group.

(i) At. size of Ga = At. size of Al, due to transition contraction.

(ii) In transition elements nuclear charge increases by 1.

(iii) but e^- enters in (n −1)d orbital exerts screening effect.

(iv) Screening effect of (n −1)d e^- balance the nuclear charge by 85%

(v) Z_{eff} on increasing each electron = 1 − 0.85 = 0.15

(vi) Increase in nuclear charge is only 0.15 so atomic size remains almost constant.

Period \ Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H ~0.30																H ~0.30	He 1.20*
2	Li 1.23	Be 0.89											B 0.80	C 0.77	N 0.75	O 0.73	F 0.72	Ne 1.60*
3	Na 1.57	Mg 1.36											Al 1.25	Si 1.17	P 1.10	S 1.04	Cl 0.99	Ar 1.91*
4	K 2.03	Ca 1.74	Sc 1.44	Ti 1.32	V 1.22	Cr 1.17	Mn 1.17	Fe 1.17	Co 1.16	Ni 1.15	Cu 1.17	Zn 1.25	Ga 1.25	Ge 1.22	As 1.21	Se 1.14	Br 1.14	Kr 2.00*
5	Rb 2.16	Sr 1.91	Y 1.62	Zr 1.45	Nb 1.34	Mo 1.29	Tc –	Ru 1.24	Rh 1.25	Pd 1.28	Ag 1.34	Cd 1.41	In 1.50	Sn 1.40	Sb 1.41	Te 1.37	I 1.33	Xe 2.20*
6	Cs 2.35	Ba 1.98	La 1.69	Hf 1.44	Ta 1.34	W 1.30	Re 1.28	Os 1.26	Ir 1.26	Pt 1.29	Au 1.34	Hg 1.44	Tl 1.55	Pb 1.46	Bi 1.52	Po	At	Rn
7	Fr	Ra	Ac															

Covalent radius of the elements (In Å)

ISOELECTRONIC SERIES

A series of atoms, ions and molecules in which each species contains same number of electrons but different nuclear charge is called isoelectronic series.

	N^{3-}	O^{2-}	F^-	Ne	Na^+	Mg^{2+}
Number of e^-	10	10	10	10	10	10
Number of p	7	8	9	10	11	12

(a) Number of electrons is same.

(b) Number of protons is increasing.

(c) So the effective nuclear charge is increasing and atomic size is decreasing. In an isoelectronic series atomic size decreases with the increase of charge.

Some of the examples of isoelectronic series are as under.

S^{2-}, Cl^-, K^+, Ca^{2+}, Sc^{3+} SO_2, NO_3^-, CO_3^{2-} N_2, CO, CN^- NH_3, H_3O^+