PERIODIC TABLE

Arrangement of known element in horizontal rows and in vertical column in such a way that elements of similar properties are grouped together in one vertical column.

Development of Periodic Table :

(i) Dobereiner low of triads:

Triads: The atomic mass of middle element is the avg. of 1st & 3rd element.

Li^{7}

Na^{23} $\quad \frac{7+39}{2} = \frac{46}{2} = 23$

K^{39}

Triads: (Li, Na, K) (Be, Mg, Ca) (Ca, Sr, Ba) (K, Rb, Cs)
(P, As, Sb) (S, Se, Te) (Cl, Br, I)

Drawback: Not applicable for all element.

(ii) Newland law of octave:

Base : Increasing order of atomic mass

Low : Properties of 1st and 8th elements are almost similar.

						H
Li	Be	B	C	N	O	F
Na	Ma	Al	Si	P	S	Cl
K	Ca					

Drawback:

(i) Applicable only upto Ca.

(ii) discovery of inert gas leads to faliure.

(iii) Lother meyer :

Curve between atomic mass and atomic volume.

Advantage: Elements of similar properties finds similar position e.g. alkali metals finds top position on curve, alkaline earth metals on descending position, halogen are on ascending position.

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(iv) Mendeleev's Periodic Law :

Physical & chemical properties of elements are the periodic function of atomic mass.

Characteristics :

(i) 8 group (I to VIII)

(ii) I to VII group divides into A & B

(iii) A sub group - Normal element

(iv) B sub group & VIII - Transition element

Advantage:

(i) Study of element become easy.

(ii) Prediction of elements : four elements named EKA.

EKA Boron ⟶ Scandium
EKA Al ⟶ Gallium
EKA Si ⟶ Germanium
EKA Mn ⟶ Technitium

(iii) Correction of doubtful masses: Atomic mass of three elements (U, Be, In) were corrected.

Drawback :

(i) Position of hydrogen : Not fixed can be placed in IA & VIIA.

(ii) Position of Isotopes.

(iii) **Anomalous Pair:** Where increasing order of atomic mass not considered.

$$\left[\underset{39.9}{\mathrm{Ar}},\ \underset{39.1}{\mathrm{K}}\right]\left[\underset{58.9}{\mathrm{Co}},\ \underset{58.6}{\mathrm{Ni}}\right]\left[\underset{127.5}{\mathrm{Te}},\ \underset{127}{\mathrm{I}}\right]\left[\underset{232}{\mathrm{Th}},\underset{231}{\mathrm{Pa}}\right]$$

(iv) Similar property elements find position in different group.

(v) Different property elements find position in same group.

(vi) Could not explain why the property of element repeated after a regular interval.

(v) Mosely's peridoic table : Charged from atomic mass to atomic number.

(vi) Modern periodic law : The physical and chemical properties of the elements are periodic functions of their atomic numbers". The atomic number is equal to the number of electrons or protons in a neutral atom."

Characteristics: (group zero) of inert gas included in the periodic table.

Advantage:

(i) Position of isotopes resolved

(ii) Short coming of anomalous pair resolved.

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Drawbacks:

(i) Position of hydrogen.

(ii) Problem of periodic function. could not be solved.

(vii) Long form of periodic table :

(Given by Bohr-Bury & Rang-Werner)

Based on electronic configuration of outermost shell.

Achievement : Electronic configuration of outermost shell of elements repeats at regular interval i.e. why property repeats.

Characteristics : Having 18 group & 7 periods.

Period	n	Sub shell	No. of Elements	Element	Name of Period
1.	1	1s	2	${}_1H$, ${}_2He$	Shortest
2.	2	2s, 2p	8	${}_3Li$ – ${}_{10}Ne$	Short
3.	3	3s, 3p	8	${}_{11}Na$ – ${}_{18}Ar$	Short
4.	4	4s, 3d, 4p	18	${}_{19}K$ – ${}_{36}Kr$	Long
5.	5	5s, 4d, 5p	18	${}_{37}Rb$ – ${}_{54}Xe$	Long
6.	6	6s, 4f, 5d, 6p	32	${}_{55}Cs$ – ${}_{86}Rn$	Longest
7.	7	7s, 5f, 6d	26	${}_{87}Fr$ – ${}_{118}Uuo$	Incomplete

IUPAC Nomenclature

(a) IUPAC gave names to elements above atomic No. 100 as follows :-

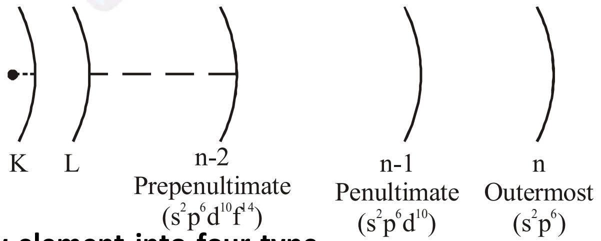
0	1	2	3	4	5	6	7	8	9
nil	un	bi	tri	quad	pent	hex	sept	oct	enn

(b) In all the elements suffix is - ium.

STUDY OF LONG FORM OF PERIODIC TABLE

Classification of elements :

(A) Bohr Classification : Based on electronic configuration.



Classify element into four type

(I) Noble gas :

(a) Element in which outermost/ultimate shell is completely filled.

(b) General configuration - ns^2np^6

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(c) Present in ‘0’ group & from 1st to 6th period.

(d) Total element 6 (He, Ne, Ar, Kr, Xe, Rn)

(II) Normal or representative element

(a) Element in which outermost/ultimate shell is incomplete.

(b) General configuration $ns^{1-2}np^{0-5}$

(c) Element of ‘A’ subgroup of mendeleev & from 1st, 2nd and 13th to 17th group in the long form of periodic table.

(III) Transition elements:

(a) Element in which ultimate as well as penultimate shell are incomplete either in ground state as well as in ionic state.

(b) ‘B’ subgroups & VIII group of Mendeleev & from 3rd to 12th group of long form of periodic table belongs to transitional element.

(c) According to this concept Zn, Cd, Hg, Uub are not transitional element.

(d) General electronic configuration = $ns^2(n-1)d^{1-10}$

(IV) Inner transition elements

(a) Element in which ultimate (n), penultimate (n–1) & prepenultimate (n–2) all the three shells are incomplete.

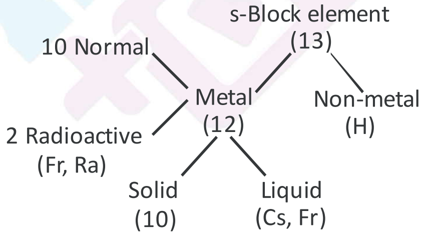
(b) Elements of IIIB(except La, Ac) are known as Inner transition elements.

(c) Total elements (28)

(B) Classification based on last electron entry :

(I) s-Block elements : Last electron enters in s-subshell. Lies in two group 1st/IA and 2nd/IIA & period from 1st to 7th.

General formula ns^{1-2}.



H is not considered as true s block element and Be is not considered as true alkaline earth metal

(II) p-block elements : in which last electron enters in p-subshell. Electronic configuration - $ns^2\ np^{1-6}$ IIIA to ‘0’ group or 13th to 18th group & from period 2nd to 7th.

Total element - 30 In this block metal, non metal & metalloid are present.

(III) d-block elements : in which last electron enters in d-subshell.

Lies in between 3rd to 12th group.

Period 4th to 7th.

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General configuration $(n-1)\,d^{1-10}\,ns^2$
Except for palladium.

(IV) f-block elements : f -block last electron enters in f-subshell.

Lies IIIB/3rd group & period 6th to 7th period.

General configuration - $(n-2)f^{1-14}\,(n-1)d^{0-1},\,ns^2$

Total element 28

14 Lanthanoids - found rarely on earth.

14 Actinoides - All are radioactive.

Determination of Period, block and group of an element

Period Number : Maximum principal quantum number in the electronic configuration of an element denotes period number.

Block number : Can be decided by last e^- entrance.

Last e^- enters in

s-subshell - s-block
p - subshell - p-block
d-subshell - d-block
f - subshell - f-block

Group number :

(A) s-block element:

Group number = Number of electron in ns subshell.

(B) p-block element:

Group number = Number of electron in np subshell + 10.

(C) d-block element :

Group No. = Number of electron in (n-1) d subshell +2.

(D) f-block element : Group No. - IIIB/3rd

Periodicity :

Regular gradation in properties from top to bottom in a group and from left to right in a period. Cause of periodicity : Due to repeatition of same outermost shell configuration coming at regular internal.

Periodic Properties :

There are two type of periodic properties.

(I) Atomic properties : Properties shown by individual atom i.e. valency, I.P., E.A., E.N. and atomic radius.

(II) Molecular property : Properties shown by molecule i.e. density, M.P. & B.P.

Note : In this chapter we will discuss about atomic properties only.

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(I) Atomic Properties :

Valency : Combining capacity of an atom.

Two concept :

(a) Old concept (i) w.r.t. 'H' & 'Cl'
(ii) w.r.t. 'O'

w.r.t. H & Cl valency of an element in a period initially increases from 1 to 4 & then decrease to 1.

w.r.t. 'O' along the period increases from 1 to 7.

(B) New concept (electronic concept) :- The number of electron required to gained or donated to achieve the nearest inert gas configuration.

For Example: Na = $1s^2, 2s^2, 2p^6, 3s^1$ → one electron required to donate i.e. valency = 1

Cl = $1s^2, 2s^2\ 2p^6, 3s^2\ 3p^5$ → One electron required to gain i.e. valency = 1

Valency in a group remains same.

(II) Screening effect/shielding effect : –

Repulsive force created by inner electron on a last electron is known as screening effect. In single electron system screening effect is absent.

Slater : Rule of calculation of screening constant (σ).

(a) ns, np e^- = 0.35
(b) (n–1) s, p = 0.85, (n-1) d & f → 1
(c) (n–2) s, p, d, f = 1.0
(d) (n–3) & all innershell = 1.0

Calculation of σ

[(Number of electron in (n^th^ shell - 1) × 0.35 + number of electron in (n–1) shell × 0.85 + number of electron in (n–2) shell & all inner shell × 1]

Variation σ, along the period & down the group increases.

Order of σ : s > p > d > f

(III) Effective nuclear charge (Zeff)

Net nuclear attraction force exert by nuclei on a valence electron is known as Zeff.

$$\boxed{\text{Zeff} = Z - \sigma}$$

For single e^- species = $\boxed{\sigma = 0}$

$$\boxed{Z_{\text{eff}} = Z}$$

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Variation :

(a) Along the period

(i) Normal elements:

Z increases by 1

σ increases by 0.35

Zeff increases by 0.65

(ii) d-block :

Z increases by 1
σ increases by 0.85
Zeff increases by 0.15

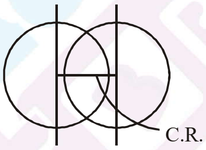
(b) Down the group : Remains constant.

(IV) Atomic radii : Average distance between nucleus & valence electron cloud. Accurate value of atomic radii cannot be measured due to
(i) Isolation of atom is quite difficult.

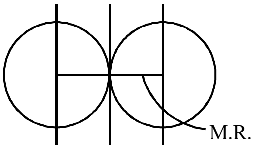
Type of Radii

(a) Covalent radii(C.R.)
(b) Metallic radii (M.R.)
(c) Vander waal radii (V.W.R.)
(d) Ionic radii (I.R.) $\begin{Bmatrix}\text{Cationic radius}\\ \text{Anionic radius}\end{Bmatrix}$

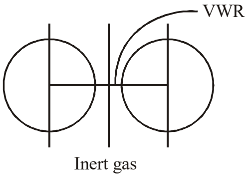
(a) Covalent radii : Half of the internuclear distance. when two homo atom bonded together with single bond.



(b) Metallic radii : Also called as crystal radii. Half of the inter nuclear distance when two adjacent atom (metal) bonded together with metallic bond.



(c) Vander waal radii : Half of the internuclear distance between two non-bonded atom of a inert gas. Vander waal radii greater than a covalent radii



VWR > 2 × C.R.

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(d) Ionic radii:

(a) Cationic radii : Cation is always smaller than its parent atom due to.

(i) Outermost shell is removed.

(ii) Increased Zeff to remaining electron.

$Mn^{+7} < Mn^{+4} < Mn^{+2} < Mn$

(b) Anionic radii : Anion is always more then its parent atom due to increases in σ & decrement in Zeff.

Isoelectronic sepecies:

Anion > neutral > Cation

$O^{-2} > F^{-} > Ne > Na^{+} > Mg^{+2}$

Variation

(a) Along the period : Radius decreases.

(b) Down the group : Radius Increases.

Imp. In each period max. measured Atomic radii- Inert gas

In each period Max. Masured covalent radii - Alkali metal

In d-block along the period, Initially atomic size decreases & constant & then increases due to increment in σ.

Exception : $B < Al \underset{\downarrow}{\simeq} Ga < In \underset{\downarrow}{\geq} Tl$

Due to transition Contraction

Due to lanthanide Contraction

Size of 4d $\approx$ Size of 5d due to lanthanide contraction.

Factor Affecting atomic size

(i) Number of shells $\propto$ atomic size

(ii) $\text{Zeff} \propto \dfrac{1}{\text{atomic size}}$

(iii) $\text{Magnitude of +ve charge} \propto \dfrac{1}{\text{atomic size}}$

(iv) Magnitude of –ve charge $\propto$ atomic size.

Ionisation Potential

Sufficient amount of energy required to remove most loosely bonded outermost shell electron from an isolated gaseous atom.

$M_{(g)} + E \longrightarrow M^{+} + e^{-}$

Property of metal.

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Tendency to form cation.

Always an endothermic process.

Successive I.P.

$IP_3 > IP_2 > IP_1$, Due to increment in Zeff.

Factors affecting I.P.

(i) I.P. $\propto$ Zeff.

(ii) I.P. $\propto \frac{1}{\text{atomic size}}$

(iii) I.P. $\propto$ Magnitude of +ve charge

(iv) I.P. $\propto \frac{1}{\text{Magnitude of –ve charge}}$

(v) Stability of Half filled & fully filled orbital → half filled due to p^3, d^5, f^7 or fully filled s^2,p^6,d^{10}, f^{14} are more stable i.e. why more amount of energy is required to remove electron so I.P. is more.

For ex. I.P. of 'N' > I.P. of 'O'

Inert gas has maximum I.P. in respective period.

(vi) Pentration power : s > p > d > f

IP of Mg > IP of Al

IP of Be > IP of B

Periodicity :-

(i) Along the period I.P. generally increases.

Except : IIA > IIIA, VA > VIA

(ii) Along the group I.P. Generally decreases.

Except : last two element due to Lanthanoid contraction.

Application of I.P. :

(i) Metallic character $\propto \frac{1}{\text{I.P.}}$

(ii) Reactivity of metal $\propto \frac{1}{\text{I.P.}}$

(iii) Basic character $\propto \frac{1}{\text{I.P.}}$

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(iv) Number of valence electron : Number of valence electron can be predicted by counting lower value of successive I.P.

Number of valence electron = Number of lower I.P. value.

Electron Affinity/(Electron gain enthalpy) (ΔegH)

Amount of energy released or absorb when an electron is added a to neutral isolated gaseous atom.

$$X_{(g)} + e^- \longrightarrow X_{(g)}^-$$

EA_1 = exothermic generally (+Ve E.A,)

EA_2 = endothermic

Inert gas has +ve value of Δeg H. Due to stable configuration.

Formation of polynegative ion is always an endothermic.

Factors :

(i) Size $\propto \frac{1}{\text{E.A.}}$

(ii) Zeff $\propto$ E.A.

(iii) Stable configuration : Be, N & inert gas have a very low value of EA due to stable configuration.

$$\begin{tikzcd}
\text{Max.} & \text{stable configuration} \arrow[l, "IP"'] \arrow[r, "EA"] \arrow[d, "EN"] & \text{min} \\
& \text{Unaffected} &
\end{tikzcd}$$

Variation :-

(a) –Along the period size ↓ EA ↑

– Along the period ΔegH becomes more –ve.

– In each period halogen has a maximum E.A. due to more Zeff.

(b) Down the group size ↑EA↓

Exception :

EA of 2nd period < EA of 3rd period.

Imp. : Max. E.A. → Cl

$$X_{(g)} + e^- \underset{IP}{\overset{EA}{\rightleftharpoons}} X^-_{(g)} + E$$

$$\boxed{\text{EA of X = IP of X}^-}$$

ELECTRONEGATIVITY

Tendency of a bonded atom to attract shared pair of electron towards itself.

Unit less property.

No energy released or absorbed.

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Factor :

(i) EN $\propto$ Zeff (ii) EN $\propto \frac{1}{\text{Atomic size}}$

Periodicity :

Along the period Zeff ↑ EN ↑

Down the group atomic size ↑ EN ↓

Max. EN –F

Min. EN –Cs

Inert gas has zero value of EN

Exception : EN scale Zn < Cd < Hg

According to Mulliken scale:-

$$\boxed{X_m = \frac{IP + EA}{2}} \qquad \boxed{2X_m = -IP - EA = 0}$$

Relation between X_m & X_p :-

$$\boxed{X_p = \frac{X_m}{2.8}}$$

According to Pauling scale:-

$$x_A - x_B = 0.028\ [\sqrt{E_{A-B} - (\sqrt{E_{A-A} \times E_{B-B}})}]$$

x_A = Electronegative of A

x_B = Electronegative of B

E_{A-B} = Bond energy of A and B

E_{A-A} = Bond energy of bond A

E_{B-B} = Bond energy of bond B.

Calculate electronegativity

Allred Rochow formula for calculating

$$EN \Rightarrow X_E = 0.359 \times \frac{Z_{eff.}}{r^2(\mathring{A}^2)} + 0.744$$

Where, $z_{eff} = z_{effective}$ (effective number charge)

Application of Electronegativity

(i) Nature of element

EN $\propto$ Non metallic element EN $\propto \frac{1}{\text{Metallic element}}$

(ii) Bond length $\propto \frac{1}{\Delta EN}$

$$\boxed{d_{A-B} = r_A + r_B - 0.09(\Delta EN)}$$

Schoemaker & Stevenson law

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(iii) Bond strength $\propto \Delta EN$

(iv) Bond energy $\propto \Delta EN$

(v) Acidic character of Hydride $\propto \frac{1}{\Delta EN}$

Basic character of hydride $\propto \Delta EN$

(vi) Nature of Oxide

Basic nature $\propto \Delta EN$

Acidic Nature $\propto \frac{1}{\Delta EN}$

(vii) % ionic character $\propto \Delta EN$

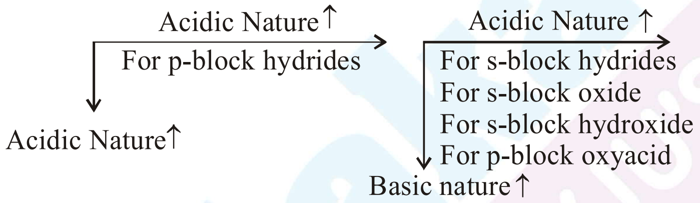
% I.C. = $16 (\Delta EN) + 3.5 (\Delta EN)^2$

(viii) Acidic strength of oxy acid $\propto$ EN of central atom.

(ix) Lewis base strength $\propto \frac{1}{EN}$

(x) Bond polarity $\propto \Delta EN$

In short :



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CHEMICAL BONDING

Introduction :

Force of attraction exist between various atoms to hold them in a molecule.

Reason for chemical bonding : To attain the maximum stability (inert gas configuration)

Condition for Chemical bonding :

(a) Force attraction > force of repulsion

(b) Potential energy should be minimum

Lewis octet rule : Every atom try to attain $8e^-$ in their outermost oribt next to the nearest inert gas configuration by donating, gaining or sharing the electron.

Exception of Lewis law :

1. Electron deficient molecule : Compound in which central atom has less then $8e^-$ in its valence shall.

For example BeF_2, $BeCl_2$, BeI_2, BH_3, BF_3, BCl_3, BBr_3,, $AlCl_3$ etc.

2. Electron rich molecule : Compound in which central atom has more then $8e^-$ in the outermost shall.

For example IF_7, SF_6, PCl_5, XeF_6 etc.

3. Odd electron molecule: The compound in which central atom has odd number of electron in their valence shall. e.g. NO, ClO_2, NO_2.

4. H, He, Li, never obeyed octet rule.

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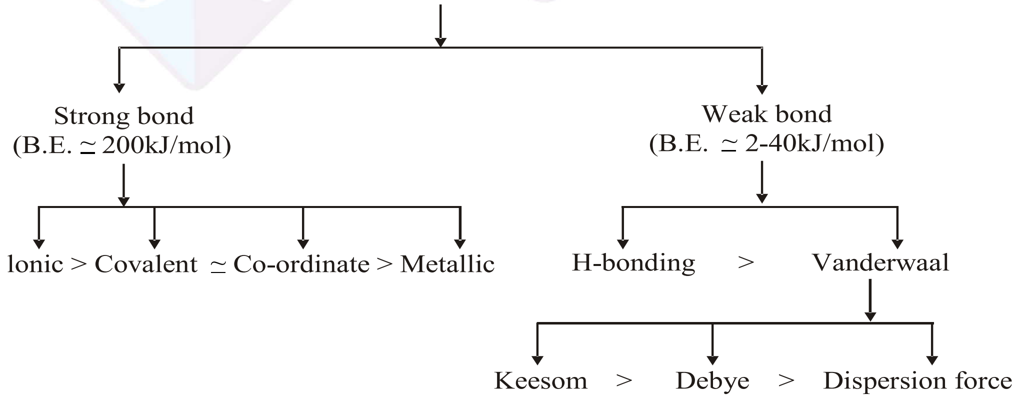

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Ionic bond :

(a) Bond between cation & anion.
(b) Bond between metal & non-metal.
Except : LiCl, $MgCl_2$, $AlCl_3$, BeO etc.
(c) $\Delta EN > 1.7$

Condition for Ionic Bond formation :

(a) Size of metal should be large
I.P. should be low.
(b) Size of non-metal should be small.
E.A. should be more.
(c) Lattice energy should be high.

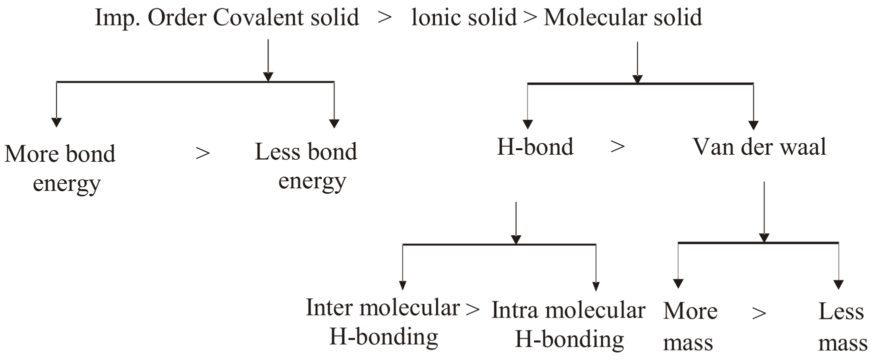
Energy involved in ionic bond formation (Born haber cycle)

ΔH = (S.E.+I.E. + D/2) – (EA +U)
= (Total energy absorbed) – (Total energy released)
For bond formation ΔH =– ive (exothermic process)

Properties of ionic Compound:

1. **Physical state**: Due to strong electrostatic force of attraction between cation & anion these compounds are hard, crystalline & brittle.
2. **Isomorphism:** Two compounds are said to isomorphs if they have similar number of electron i.e. similar configuration aof cation & anion.
   e.g. [NaF, MgO] [$CaCl_2$, K_2S]

Melting point & boiling point: High M.P. & B.P. due to presence of strong electrostatic force between ions.
Covalent solid like SiO_2, B_4C, have more m.p. due to 3-D giant network.
Ionic solid like NaCl, Al_2O_3, have more m. p. due to high lattice energy.
Molecular solid like CO_2 have least melting point due to presence of weak van der waal force.
M.P. & B. P.



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If molecular mass of two covalent compound are same then ΔEN will be consider.

Imp. order $LiH > NaH > KH > CsH$

$MgO > CaO > BaO$

$LiCl < NaCl > KCl > RbCl > CsCl$

$LiF > NaF > KF > RbF > CsF$

$Li_2O > Na_2O > K_2O > Rb_2O > Cs_2O$

Among metal halide, fluoride has maximum m.p.

$LiF > LiCl > LiBr > LiI$

$NaF > NaCl > NaI$

Solubility : Ionic compounds are souble in polar solvent like water.

Factor affecting solubility:

(i) Dielectric constant α solubility

(ii) Lattice energy $\alpha \frac{1}{\text{solubility}}$

(iii) Hydration energy α solubility

For any compound to be soluble in water

$\boxed{\text{Hydration energy} > \text{Lattice energy}}$

Imp. order:

No compound is 100% ionic. Every compound contain some covalent charactor due to polarization

Due to strong electrostatic force of attraction between cation & anion electron density of anion becomes more in between two ions & covalent character is developed.

$\boxed{\text{Covalent character} \propto \text{Polarization} \propto \text{Zeff of cation}}$

Polarization power (Ionic potential) : capacity of cation to polarize anion represented by (ϕ)

$$\boxed{\phi \propto \frac{\text{Charge on cation}}{\text{Size of cation}}}$$

Polarisability : Tendency of an anion to get polarized by cation.

Factor affecting polarization (fajan's rule)

(i) Charge on cation/anion $\propto$ polarization α covalent character

(ii) Size of cation $\propto \frac{1}{\text{Polarization}} \propto \frac{1}{\text{Covalent Character}}$

(iii) Size of anion $\propto$ polarization α covalent character

(iv) Pseudo inert gas configuration : Cation having pseudo inert gas configuration (i.e. 18 electron in outermost shall have more polarization power due to high Zeff.

$CuCl > NaCl$ (Covalent Character)

[due to poor shielding effect of d e^- in Cu^{+1}]

Some important facts :

(i) Sulphides are less soluble in water than oxides of metal.

(ii) Li salts are soluble in organic solvents.

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Polarization increases Covalent character
M.P. decreases →
NaF > NaCl > NaBr > NaI
$NaCl > MgCl_2 > AlCl_3$
$BaCl_2 > SrCl_2\ CaCl_2\ MgCl_2 > BeCl_2$

Covalent bond :
Bond between two highly electronegative element
Mutual sharing of electron takes place.

Orbital Concept of Covalent Bond :

An orbital can accomodate at the most 2 electrons with opposite spin.
Only those orbitals will participate in bond formation which have unpaired electron.
Empty orbital accepts two electrons to complete the orbital.
Due to presence of vacant d-orbital elements can expand their octet in the presence of highly eletronegative element like F, Cl, O, N etc.
PCl_5, SF_6, IF_7, is possible but NCl_5, OF_6, are not possible.
PF_5, PCl_5, are possible but PH_5, is not.
An element which has even valency will always show even valency in excited state.
PCl_4, SF_3, SF_5 are not possible but PCl_3, PCl_5, SF_2, SF_4 & SF_6 are possible.
⇒ Short coming : Could not provide in formation regarding shape of molecule & strength of bonds.

Wave Mechanical Model

Two Model :
(i) Valence bond theory (VBT)
(ii) Molecular orbital theory (MOT)

(1) Valence bond theory:
Given by Heitler & London Extended by pauling & Slater.
Strength of bond α Extent of overlapping.
Extent of overlapping depends on two factors.

(i) Nature of orbital:
(a) directional orbital : p, d & f (more extent of overlapping)
(b) non- directional orbital : s (less extent of overlapping)
order of overlapping $\boxed{p-p > s-p > s-s}$
Exception $\boxed{1s-1s > 2p-2p}$
Nature of overlapping :
(a) Co-axial overlapping (Along the internuclear axis)
(b) Perpendicular to internuclear axis
Extent of overlapping is maximum, σ–bond is formed.
π-bond is formed after σ–bond.

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For maximum bond strength :-
(i) Lower value of principal quantum number.
(ii) σ is stronger than π (when value of n is same)
(iii) Directional nature (when type of overlapping is same)

Limitation :
(i) Does not define the shape of the molecule.

Hybridisation (Pauling & Slater)
Imaginary concept
Mixing of different shape and approximate equal energy atomic orbital to give new orbital of same shape.
Hybrid orbitals always forms σ–bond. (Except - Benzyne)
In hybridization all type of orbitals can precipitate.
(Vacant, Half-filled or Fully filled)
Number of hybrid orbital formed will be equal to the number of atomic orbitals taking part in hybridization.

Valence shell electron pair repulsion theory (VSEPRT):

Given by Gillespie & Nyholm
Defines the shape of molecule

Case-I Molecules in which central atom do not have any lone pair are called symmetric structure & their shape will be according to their hybridization.

Case-II Molecules in which central atom has lone pair are known as asymmetric structure, In this case lone pair should be kept at that position where lone pair exerts minimum repulsive force.
Order of reqlusion : L.P. – L.P . > L.P. – B.P. > BP. – B.P.

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TYPES OF HYBRIDIZATION & POSSIBLE STRUCTURE

Type of Hybridization	No. of B.P.	No. of L.P.	Shape	Examples
1. sp-hybridization	2	-	Linear	BeF_2, CO_2 CS_2, $BeCl_2$
2. (a) sp^2-hybridization	3	-	Trigonal planar	BF_3, $AlCl_3$, BeF_3^-
(b) sp^2-hybridization	2	1	V-shape Angular	NO_2^-, SO_2, O_3
3. (a) sp^3-hybridization	4	0	Tetrahedral	CH_3, CCl_4, PCl_4^+, ClO_4^-, NH_4^+, BF_4^{-2} SO_4^{-2}, $AlCl_4^-$
(b) sp^3-hybridization	3	1	Pyramidal	NH_3, PF_3, ClO_3^-, H_3^+O, PCl_3, XeO_3, $N(CH_3)_3$, CH_3^-
(c) sp^3-hybridization	2	2	V-shape, Angular	H_2O, H_2S, NH_2^-, OF_2, Cl_2O, SF_2, I_3^+
4. (a) sp^3d-hybridization	5	-	Trigonal bipyramidal	PCl_5, SOF_4, AsF_4^-,
(b) sp^3d-hybridization	4	1	See Saw,	SbF_4^-, XeO_2F_2
			folded square distorted tetrahedral	SbF_4^- , XeO_2F_2
(c) sp^3d-hybridization	3	2	almost T-shape	CIF_3, ICl_3
(c) sp^3d-hybridization	2	3	Linear	I_3^-, Br_3^-, ICl_2^-, ClF_2^- , XeF_2
5. (a) sp^3d^2-hybridization	6	-	Square bipyramidal/ octahedral	PCl_6^- , SF_6
(b) sp^3d^2-hybridization	5	1	Square pyramidal/ distorted octahedral	$XeOF_4$, ClF_5, SF_5^- XeF_5^+
(c) sp^3d^2-hybridization	4	2	Square planar	XeF_4
6. (a) sp^3d^3-hybridization	7	-	Pentagonal bipyramidal	IF_7
(b) sp^3d^3-hybridization	6	1	Pentagonal pyramidal/ distorted octahedral	XeF_6
(c) sp^3d^3-hybridization	5	2	Pentagonal planar	XeF_5

Co-ordinate bond

This type of bond is formed by one side sharing of pair of electron between atoms. Electron pair of one atom is shared between two atom.

Atom which provide lone pair for sharing is called donor.

Atom which accepts electron pair is called acceptor.

Shown by '→' & direction is from donor to acceptor.

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Necessary condition :

Acceptor should have vacant orbital.

Donor should have complete octet.

Example :

(i) Protonation : $H_2O \rightarrow H_3O^+$, $NH_3 \rightarrow NH_4^+$, $N_2H_4 \rightarrow N_2H_5^+$

(ii) Polymerization : $AlCl_3 \rightarrow Al_2Cl_6$, $BeCl_2 \rightarrow (BeCl_2)_n$

During the formation of coordinate bond, structure & shape of the molecule gets changed.

Dipole moment (μ)

Measure the polarity in molecule (μ) = $q \times d$

Unit debye = esu - cm

1 Debye = 10^{-10} esu-cm.

Homonuclear diatomic H_2, N_2, O_2, F_2, ($\mu = 0$) → non- polar

Heteronuclear diatomic ($\mu \propto \Delta$ EN) HF > HCl > HBr > HI

Polyatomic molecule resultant dipole moment is a vector addition of dipole moment of various bond.

$$\overleftarrow{O}=C=\overrightarrow{O} \quad \mu = 0 \quad \text{non}-\text{polar}$$

Imp. order

(a) $NH_3 > NI_3 > NBr_3 > NCl_3 > NF_3$

(b) $NH_3 > SbH_3 > AsH_3 > PH_3$,

(c) HF > HCl > HBr > HI

(d) $H_2O > H_2S$,

(e) $CH_3Cl > CH_3F > CH_3Br > CH_3I$

(f) $CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4 = CH_4$

Application :

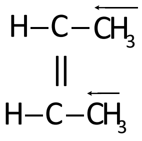
(i) Predict shape & polarity of molecule

If central atom contain lone pair than $\mu \neq 0$, moelcule will be polar & unsymmetrical shape.

If central atom surrounded with all identical atom then $\mu \neq 0$, molecule non-polar.

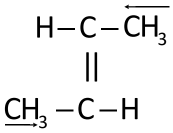
(ii) Distinguish between cis & trans form

$\mu_{cis} > \mu_{trans}$



Additive

$\mu \neq 0$



Substractive

$\mu = 0$

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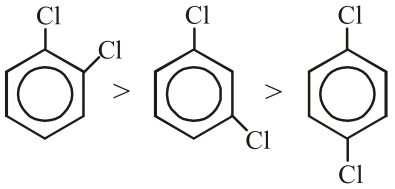
(iii) To find out dipole moment of a substituent of benzene ring.



$$\boxed{\mu \propto \frac{1}{\text{bond angle}}}$$

H-bonding

Given by Latimer & Rodebush.

Electrostatic force of attraction between H & highly electronegative atom.

This is intermolecular force. i.e. why exist only in covalent molecule.

Also known as dipole-dipole attraction.

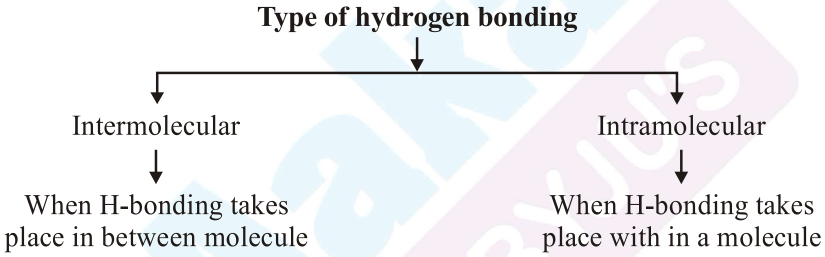
Necessary conditions :

(i) Hydrogen should be covalently bonded with highly electronegative element.

(ii) Highly electronegative element should have EN ≥ 3.

(iii)Hydrogen bonding is possible only in those moelcule in which H is directly attached with F, O, N,

$$\boxed{\text{Strength of H} - \text{bond} \propto \text{EN of highly electronegative element}}$$



Strength of intermolecular H-bond > Intramolecular H-bond.

Imp. Intramolecular H-bonding taking place only in ortho-derivative of aromatic compound.

Application :

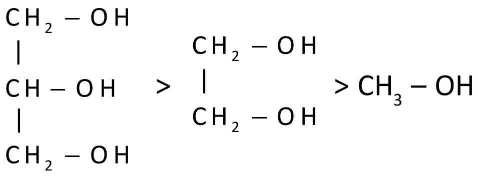
(i) Physical state : H_2O is liquid H_2S gas.

HF is liquid HCl gas.

(ii) M.P. & B.P. : Due to presence of H-bonding M.P. & B.P. increases M.P. of alcohol > M.P. of thiol

(iii) Volatility : M.P. & B.P. ↑ volatility ↓

(iv) Viscosity & Surface tension :



$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} > \begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} > CH_3-OH$$

(v) Solubility in H_2O : Any organic compound which get dissolved in H_2O is due to H-bonding.

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Extent of solubility $\propto$ H-bonding

(vi) Association of molecule :

KHF_2 is possible but not KCl_2. $[K^+ + [F^- \underset{\text{(H.Bond)}}{..........} H–F]$

MOLECULAR ORBITAL THEORY

Imaginary concept

Given to explain

(i) Paramagnetic nature of O_2 molecule.

(ii) Existence of species like $H_2^+ . H_2^-$ & species having fractional bond order.

Main point of M.O.T.

(a) Atomic orbital represented by ψ (wave function) participate to form molecular orbital.

(b) Z-axis is considered as main axis so p_z combination form σ moelcular orbital.

(c) The number of orbital participating in combination must have almost same energy & same symmetry. Will produce same number of orbital.

(d) Two type of molecular orbital formed.

(i) Bonding molecular (ii) Anti-bonding molecular

(e)Number of atomic orbital participating

$= \frac{1}{2}$ number of B.M.O. + $\frac{1}{2}$ number of ABMO.

(f) BMO is formed by addition of two wave function ($\psi_A + \psi_B$) when they are in same phase, represented by σ, π

(g) ABMO is formed by subtraction of two wave function ($\psi_A - \psi_B$) when they are in opposite phase, represented by σ^*, π^*.

Energy of ABMO > Energy of A.O. > energy of BMO

Imp. sequence order

for B_2, C_2, N_2 (Number of e^-'s ≤ 14) = $\sigma_{1s}, \sigma_{1s}^*, \sigma_{2s}, \sigma_{2s}^* \ (\pi_{2px} = \pi_{2py}),\ \sigma_{2pz}\ (\pi_{2px}^* = \pi_{2py}^*),\ \sigma_{2pz}^*$

B.O. of C_2 = $\frac{8-4}{2} = 2$

(It contains two π bonds with out d bond

$\because$ last four e^- enters in π B.M.O.)

for O_2, F_2, Ne_2 (Number of e^-'s > 14) = $\sigma_{1s}, \sigma_{1s}^*, \sigma_{2s}, \sigma_{2s}^*, \sigma_{2pz}\ (\pi_{2px} = \pi_{2py})\ \left(\pi_{2px}^* = \pi_{2py}^*\right), \sigma_{2pz}^*$

Significance of M.O.T. :

(a) Concept of bond order :

Bond order = $\frac{1}{2}$ $[N_b - N_a]$

N_a = number of antibonding e^-'s

N_b = number of bonding e^-'s

If $N_b > N_a$ B.O. = +ve molecule exist

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$N_b < N_a$ B.O. = –ve moelcule does not exist

$N_b = N_a$ Does not exist

(b) Stability $\propto$ B.O. α bond dissociation energy

(c) B.O. $\propto \frac{1}{\text{Bond length}}$

Iso electronic species have same bond order & have same magnetic property.

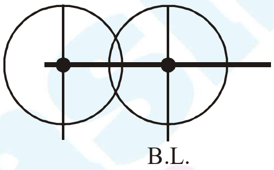
If species have fractional bond order it will always be paramagnetic.

If in two species bond order is same the stability, will be decided by counting number of antibonding e^-'s. If number of antibonding e^- more, than number of bonding e^-'s then molecule will be unstable.

Bonding parameters

Imp. points :

1. **Bond length :** Internuclear distance between two atom when they are bonded together.



Factor affecting bond length

(i) **ΔEN value**

$d_{A-B} = r_A + r_B - 0.09\,(\Delta EN)$

$\Delta EN \uparrow$ B.L. $\downarrow$

H–F < H–Cl < H–Br < H–I

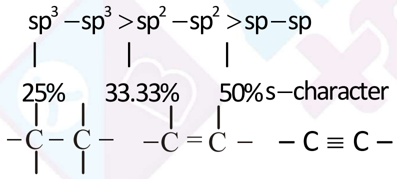
(ii) **Atomic size**

$\boxed{\text{B.L.} \propto \text{Atomic size}}$

(iii) **Bond order :** B.O. $\propto \frac{1}{\text{B.L.}}$

$\boxed{C-C > C=C > C\equiv C}$

(iv) **Hybridisation :** B.L.



$sp^3-sp^3 > sp^2-sp^2 > sp-sp$

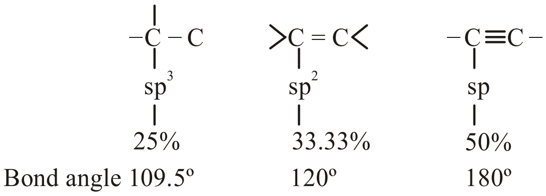
25% 33.33% 50% s–character

$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \quad -\overset{|}{C}=\overset{|}{C}- \quad -C\equiv C-$

2. **Bond angle :** The angle between any two adjacent bond is known as bond angle.

Factor affecting bond angle

(a) Hybridization : wOn increasing % s-character bond angle also increases.



$-\overset{|}{\underset{|}{C}}-C \qquad >C=C< \qquad -C\equiv C-$

$sp^3 \qquad sp^2 \qquad sp$

25% 33.33% 50%

Bond angle 109.5° 120° 180°

Case-I When hybridization is same, bonded atom are same but central atom & lone pair are different.

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$$B.A. \propto \frac{1}{\text{Number of L.P.}}$$

Example :

CH_4	$\ddot{N}H_3$	$H_2\ddot{O}:$
$\downarrow$	$\downarrow$	$\downarrow$
sp^3	sp^3	sp^3
109.5°	107°	104.5°
No L.P.	1 L.P.	2 L.P.

Case-II When hybridization is same, number of lone pair is same central atom is different & side atom are same then

$$\boxed{\text{Bond angle} \propto \text{EN of central atom}}$$

$$\ddot{N}H_3 > \ddot{P}H_3 > \ddot{A}sH_3 > \ddot{S}bH_3$$

Examle : Bond angle 107° 93° 91°

$$\xrightarrow{\hspace{5em}}$$

EN of central atom decrease
Bond angle decrease

$$H_2\ddot{O}: > H_2\ddot{S}: > H_2\ddot{S}e: > H_2\ddot{T}e:$$

$$\xrightarrow{\hspace{5em}}$$

Bond angle decreases

Case - III When hybridization is same , number of lone pair are same and central atom are same, but side atoms are different.

$$\boxed{B.A \propto \frac{1}{\text{EN of side atom}}}$$

$OF_2 < OCl_2 < OBr_2 < OI_2$ $NF_3 < NCl_3 < NBr_3 < NI_3$

Note : Symmetrical mol. having no. l.p. and same hyb. B.A. are same.

e.g (i) $BF_3 = BCl_3 = BBr_3 = BI_3$
(ii) $SO_4^{2-} = PO_4^{3-} = ClO_4^-$

Imp. point :

In ethers oxygen has sp^3 hybridization having two L.P. but still bond angle is 110° because of large size of alkyl group.

$$R-\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}-R$$

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