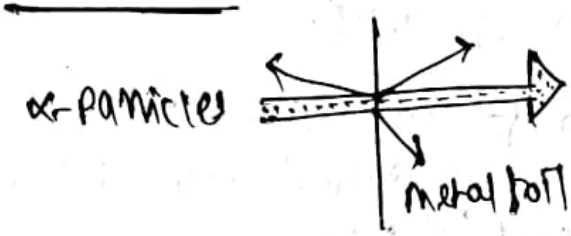
Periodic properties

Mendeleev (1834-1907) - classified elements on the basis of similarities of their properties (1864).
Properties of elements are a periodic function of their atomic weights (periodic law).
modern periodic law :- The properties of elements are periodic functions of their atomic numbers.

Early theories of atom :-

Rutherford model - α-particles bombardment



Atomic spectra - ground state to excited state energization.
line spectra
Bohrs theory - Definite energy levels within atom.
wave nature of electron :- Heisenberg uncertainty principle
De Broglie theory - electrons as particles & waves.

Quantum numbers :-

1) Principal quantum number (n) :- main energy level in the atom denoted as K, L, M, N.. or 1, 2, 3, 4... also known as shells.
2) Azimuthal quantum no (l) :- electron can be located in a region in space called as orbital.

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Subenergy levels within principal energy levels called s, p, d, f – sharp, principal, diffuse & fundamental. l represents orbitals having 0 to n-1 values.

3) Magnetic quantum no. (m) :- Due to orbital motion electron has magnetic property denoted by (m) and have values from (-l to +l). [(2l+1) m values.]

4) Spin quantum no. (s) :- electron rotates on its own axis, along with rotation it possess spin quantum no. which has +1/2 to -1/2 values depends on direction of rotation of axis.

* Electronic configuration :- 1s orbital n=1, l=0
Ground lowest energy

Aufbau (building up) Process :- level

1) Two e$^{\ominus}$ in the same atom can't have all quantum numbers same (Pauli's exclusion principle).

2) orbitals are filled with e$^{\ominus}$ with increasing energy.

1 s orbital – 2 e$^{\ominus}$
3 p orbital – 6 e$^{\ominus}$
5 d orbital – 10 e$^{\ominus}$
7 f orbital – 14 e$^{\ominus}$

3) Hund's rule :- when electrons are added to orbitals of same energy, they will fill up each of orbitals with a single electron before pairing takes place in any one orbital.

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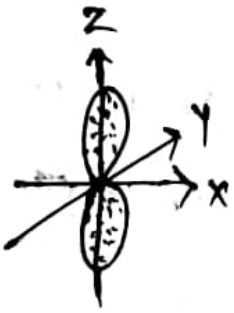
Exceptions

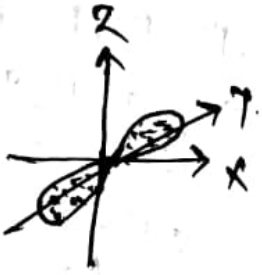
Half filled or completely filled orbitals do have lower energies.
e.g. Cr, Cu, Nb

1s

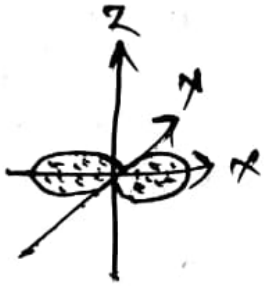
2s



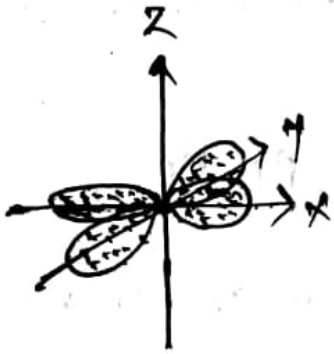
p_z



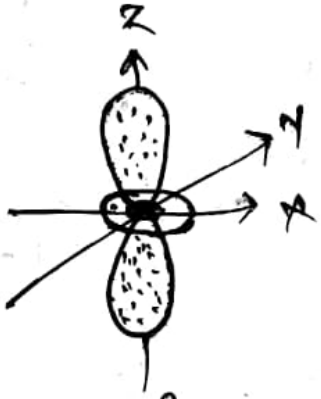
p_y



p_x

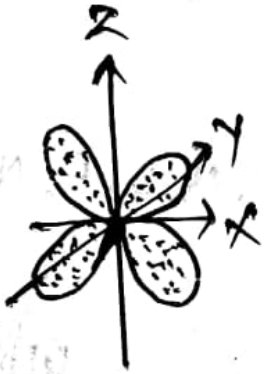


$d_{x^2-y^2}$



d_{z^2}

d_{xy}



d_{xz}

d_{yz}

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Long form of the periodic table :-

Periods :- 7 periods, outermost e⊖ conf. ns^1.

Groups :- 16 groups

* Classification of the elements on the basis of e⊖ conf.

1) S-block elements :- last e⊖ enters ns orbital of atom. group 1 and 2, valence shell conf. ns^1 to ns^2.

2) P-block elements :- last e⊖ enters np orbital of atom. group 13 to 18, exception He. 1P, 3P upto 5P & 6P.

3) d-block elements :- (n-1) d orbital (transition elements) 3d, 4d, 5d, 6d series. Electronic conf. $(n-1)d^{1-10}$, ns^1 or 2

4) F-block elements :- (n-2) f orbital (Inner transition elements)

4f and 5f series.

Electronic conf. $(n-2)f^{0-14}$, $(n-1)d^{0,1 \text{ or } 2}$, ns^2.

* Periodic Properties :- The physical and chemical properties of elements which vary steadily in a period & are repeated at definite intervals are known as P.P.

i) Effective nuclear charge
ii) Atomic & ionic radii
iii) Ionisation energy
iv) Electron affinity
v) Electronegativity
vi) Metallic non-metallic character
vii) Oxidation states etc.

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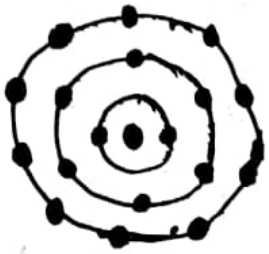
1) Effective nuclear charge :-

Screening or shielding effect - The effect of inner e⊖ on the outermost electron is known as screening or shielding effect.



$s > p > d > f$

Effective nuclear charge :- The actual charge or nuclear attraction which is felt by the outermost electron in an atom is known as effective nuclear charge (Z^*).

$Z^* = Z - S$

Z^* = Effective nuclear charge

Nuclear charge

Shielding const.

Slater rule :- Shielding const. S can be calculated using set of empirical rules.

(1s), (2s, 2p), (3s, 3p), (3d), (4s, 4p), (4f) (5s, 5p)

Each group is assigned contribution per e⊖. The sum of all such contribution that affect the e⊖ under consideration is the shielding constant.

i) zero for each e⊖ in the group (right to e⊖ considered)

ii) 0.35 for each e⊖ in the same group (n) except 1s for which contribution is 0.30.

iii) 0.85 for each e⊖ in the (n-1) group

iv) 1.00 for each e⊖ closer than (n-1) group. i.e. the

v) 1.00 for ← " ← all the lower groups. (d or f)

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Ex. 4s eΘ of K

$_{19}K = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$

Applying Slater rules :-

Effective nuclear charge felt by 4s¹ eΘ = $Z^* = Z - S$

Z = 19

S = 0.85 for eΘ in (n-1) group.

1.00 for ⟵ lower than n = 1

i.e. $Z^* = Z - S$

$= 19 - [(0.85(\text{no. of } e\Theta \text{ with } n=3) + (1.00(\text{no. of } e\Theta \text{ with } n<3))]$

$= 19 - [(0.85 \times 8) + (1.00 \times 10)]$

$= 19 - [18.8]$

$= 2.20$

∴ Z^* felt by 4s¹ eΘ in K atom = 2.20

Homework → 3d eΘ in Zn & 4s eΘ in Cu

Zn = Z^* = 8.85

Cu = Z^* = 3.70

$_{30}Zn$

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 3d^{10}, 4s^2$

$Z^* = Z - S$

$= 30 - [1.00(\text{no. of } e\Theta \text{ in lower gr.}) + (0.35 \times \text{no. of } e\Theta \text{ in 3d})]$

(18) (9)

$= 30 - 21.15$

$= 8.85$

$_{29}Cu$

$1s^2, 2s^2 2p^6, 3s^2 3p^6, 3d^{10}, 4s^1$

$Z^* = Z - S$

$= 29 - [(0.85 \times 18) + (1 \times 10)]$

$= 29 - 25.30$

$= 3.70$

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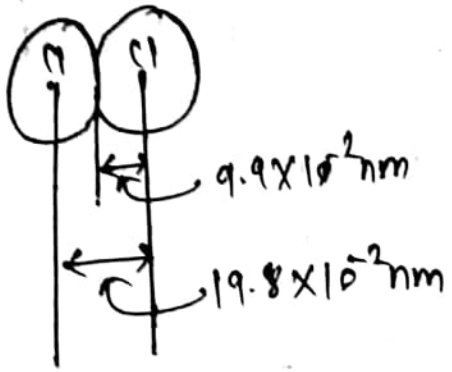
e) Atomic and ionic radii :-

Atomic radius - Distance betn nucleus & outermost e⊖.

Diatomic molecule - Internuclear distance in Cl_2



For atoms attractive forces are van der waals forces. van der waal's radii are larger than covalent radii because orbital overlap during bond formation brings atoms much closer.

Periodic trends in Atomic size :-

In the periods :- Li → Ne ~~Groups~~

Nuclear attraction on the outermost electrons increases due to which the atomic size decreases.

s/p-block elements - Effective nuclear charge increases on outermost e⊖ increases hence atomic size decreases. Thus s and p block elements shows different properties.

d-block elements - e⊖ are added to penultimate shell. Nuclear charge increases with atomic no. effective nuclear charge on outer e⊖ decreases. As a result atomic size decreases to some extent than s & p elements.

f-block elements :- e⊖ are added to pre-penultimate shell. Thus ~~less~~ screening effect of

inner electrons. Effective nuclear charge decreases than d-block elements. As a result, decrease in the atomic size amongst p-block element is extremely less. called Lanthanide or Actinide contraction.

In the groups :- $\Lambda^{Li}_{Cs}\downarrow$

Increase in atomic size with the increase in at. no. as atomic no. increases nuclear charge increases & no. of shells in atom also increases.

Ionic radii :- $M \longrightarrow M^+ + e^\ominus$ cation formation (decreases size)

metals → cations

Non metals → Anions $A + e^\ominus \longrightarrow A^\ominus$ (Increases size)

Cations are smaller than the atoms from which they are formed while anions are larger than the atom from which they are formed.

Ionic radii determined by measuring ionic bond length

In a period — No comparison / contains metals & non metals

In a group — Λ

Effect of atomic & ionic radii on properties :-

1) In a group, small cations are less basic in nature e.g. oxides of lithium are less basic than those other alkali metals.

2) Smaller ions undergo hydration to greater extent e.g. Li^+ has maximum hydration than other alkali

3) Smaller ions have greater complexing power & form

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stable complexes.

4) Chemical reactivity depends on atomic & ionic size of atoms lose, gain or share electrons which is linked to electrostatic forces of attraction betn nucleus and outer electrons.

5) The extent of ionicity depends on size of cations and anions (covalent bond).

Size of isoelectronic species :- same no. of electrons size decreases with increase in atomic number.

Na^+ Mg^{2+} Al^{3+} Si^{4+} 10 e⊖ each

At.No. 11 ← 12 ← 13 → 14

size decreases

* Ionization of atoms :-

Metals ionizes to cations by losing electrons.
Non metals ionizes to anions by accepting electrons.

Ionization energy :- The amount of energy required to remove the most loosely bound electron from an isolated gaseous atom of an element in its ground state is known as ionization energy.

Expressed as Ionization enthalpy (ΔH_{ion}) KJ/mol.

1st ionization energy - Remove 1st outer e⊖
2nd ionization energy - Remove 2nd —"—

Factors affecting magnitude of ionization energy :-

1) Size of the atom - larger size lesser attraction

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between nucleus & outermost e⊖ thus easy to remove an electron. Atomic size increases, ΔH_{ion} decreases.

2) Nuclear charge :- Greater charge, greater force of attraction bet nucleus & outermost e⊖ thus difficult to remove an electron from atom hence greater ΔH_{ion}.

3) Shielding effect of inner e⊖ :- More shielding, less nuclear attraction towards outermost e⊖ thus less effective nuclear charge hence ΔH_{ion} decreases.

shielding ability $s > p > d > f$ ΔH_{ion} decreases in the same order.

4) Nature of e⊖ conf. :- ΔH_{ion} values are high for stable configurations such as half filled and completely filled orbitals.

Periodic trends :- In a period – increases →
In a group – decreases ↓

Exceptions – B vs Be

B – $1s^2, 2s^2, 2p^1$ – less ΔH_{ion}

Be – $1s^2, 2s^2$

Homework – 1st ΔH_{ion} of oxygen atom less than N atom

* Electron affinity :- It is the energy released when an isolated atom accepts electrons to form a gaseous anion.

It is the measure of the tightness with which an additional electron is held by an atom.

Also referred as Electron Attachment Enthalpy.

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First addition of electron opposes further addition of second & third electron.

Positive values for halogen atoms & negative values for polynegative O^{2-} and S^{2-}.

Positive electron affinity value indicates that the anion is more stable than neutral atom whereas (-ve) value shows neutral atom more stable than its corresponding anion.

Factors affecting electron affinity :

1) Atomic size - Smaller size lesser distance betn added e⊖ & nucleus thus stronger attraction & hence more electron affinity.

2) Nuclear charge - Larger nuclear charge, more strongly it will attract additional e⊖ therefore more electron affinity i.e. more energy will be released.

3) Electronic conf. - Atoms with completely filled or half filled outer orbitals do not show a strong tendency to accept an extra e⊖ thus have zero or less electron affinity.

Periodic trends in electron affinity :

In a period - Li $\xrightarrow{\text{increase}}$ Ne

Halogens ns^2np^5 has (-ve) EA & forms stable anion

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with inert gas conf. ns^2np^6 by gaining an electron.

	F^-	Cl^-	Br^-	I^-	H^-	O^{2-}	S^{2-}
EA kJ/mol	349	366	343	316	74.3	-702	-332

In the groups :-

$IE(A^-) = EA(A)$ ↓ decreases

Atomic size & nuclear charge increases but Z_{eff} decreases due to increasing shielding effect of inner e⊖ thus nuclear charge is not sufficient enough to hold additional e⊖. consequently e⊖ affinity decreases down gr.

Exception - EA of F is less than that of Cl. First element of gr. should have highest EA but in case of halogens, Fluorine being smaller in size & has more electron density repulse additional e⊖ by existing e⊖ than in chlorine. Thus addition of e⊖ in fluorine becomes less favourable thus less EA than that of chlorine.

* Electronegativity :- Electronegativity of an element is its capacity to attract electrons towards it from other element in its compou shows metallic & non-metallic properties of eleme explains many properties concerning energy & distribution of charge in bonds.

Bond dissociation energy, bond polarity, Ioni Character of covalent bonds.

Expressed as Chi (χ).

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1) Pauling's method :- It is based on an empirical relation between bond energy and the electronegativities of the atoms forming the bonds.

Covalent bonds – similar electronegativities elements
Ionic bonds - large difference in electronegativities.

Covalent Heteronuclear diatomic molecule A-B, the bond dissociation energy $D_{A-B} = D_{cov}$ (pure covalent bond energy)

D_{AA} - Bond diss. energy of A_2
D_{B-B} – " – B_2

$= \frac{1}{2}[D_{A-A} + D_{B-B}]$

For ionic molecules, $D_{A-B} > D_{cov}$ by amount Δ_{A-B} called ionic covalent resonance energy or resonance energy.

$$D_{A-B} = \frac{1}{2}[D_{A-A} + D_{B-B}] + \Delta_{A-B}$$

$$\therefore \Delta_{A-B} = D_{A-B} - 1/2[D_{AA} + D_{B-B}]$$

According to pauling, electronegativity difference bet two atoms $= \sqrt{\frac{0.102}{0.088}\Delta}$

HCl, $D_{H-H} = 435$ KJ/mol, $D_{Cl-Cl} = 242.7$ KJ/mol

$D_{H-Cl} = 431$ KJ/mol

$$\Delta_{H-Cl} = D_{H-Cl} - 1/2[D_{H-H} + D_{Cl-Cl}]$$
$$= 431 - 1/2[435 + 242.7]$$
$$= 431 - 338.9$$
$$\Delta_{H-Cl} = 92.1 \text{ KJ/mol}$$

$$\therefore \chi_{Cl} - \chi_H = \sqrt{\frac{0.102}{0.088}\times 92.1} = 0.9 \quad \because \chi_H = 2.1$$

$$\chi_{Cl} = 2.1 + 0.9 = 3.0$$

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2) Mulliken's method :- Electronegativity could be regarded as the average of ionization energy & electron affinity of the element.

i.e. $\chi = (I + E)/2$

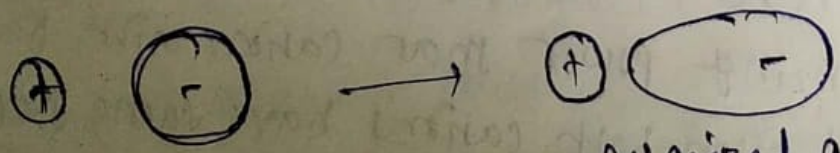
Drawback - only few electron affinity values are known.

Periodic trends in electronegativity :-

In a period - Increases →

In a group - ↓ Decreases

* Polarizability :- When cation & an anion are brought closer to their equilibrium distance, the cation tends to attract electron cloud & repels positively charged nucleus of an anion. The combined effect of these forces that electron cloud of an anion does not remain symmetrical but elongates towards the cation. This distortion is called polarization of anion by cation and anion is said to be polarized.



No distortion Polarized anion

If Polarization is less, — ionic bond formation

— " (increase) more — covalent character (small)

cations with more polarizing power & anions have more polarizability.

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Factors affecting the polarization of an ion :-

Fajan's rule - Factors affecting extent of polarization

i) **charge on the cation or anion :-** The polarizing power of a cation to polarize an anion increases with the increase in its positive charge.

Ionic $Na^+ < Mg^{2+} < Al^{3+}$ ⟶ chlorides covalent character increase from Na to Al.

Similarly, polarizability of an anion increases with the increase in its negative charge.

$F^- < O^{2-}$ oxides are more covalent than fluorides.

$LiCl > NaCl > KCl > CsCl$

ii) **Size of the cation or anion :-**

Size decreases polarizing power increases (cations)

$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+}$

Size increases polarizability increases (anions)

$F^- < Cl^- < Br^- < I^-$ $LiF < LiI$

F – Ionic

I – covalent

iii) **Electronic conf. of an cation :-**

cations with 18 e⊖ in valence shell ($ns^2np^6nd^{10}$) has greater polarizing power than cation with 8 valence e⊖ (ns^2np^6) even both cations have same size & charge.

Reason - 10 d e⊖ shield nuclear charge less effectively than s & p e⊖ of ns^2np^6 shell.

$Zn^{2+} > Mg^{2+}$ but has greater polarizing power to polarize cation.

Cu^+ – 18 e⊖ – $3s^2, 3p^6 3d^{10}$ (covalent) $CuCl$ >

Na^+ – 8 e⊖ – $2s^2, 2p^6$ $NaCl$

due to orbital overlap dispersion of charge & covalent (ionic)

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According to Fajan's rule, covalent bonding is favoured by,

1) small cation
2) Large anion
3) Large charges on either ion
4) cations having 18 $e^{\ominus}$ in its outer shell.

e.g. LiCl is covalent & NaCl is ionic due to more polarizing power of small Li

* Oxidation states :- It is a no. assigned to an element in a compound which denotes no. of $e^{\ominus}$ either removed from or added to that element.

free element — zero oxidation state
(+ve) oxidation state - Electrons are removed from atom.
(-ve) —"— - Electrons are added to an element

Sum of all the oxidn state of the various elements in a compound should be zero.

$Na \rightarrow Na^+ + e^{\ominus}$ Na^+ — (+1) oxidation state
$Fe \rightarrow Fe^{2+} + 2e^{\ominus}$ Fe^{2+} — (+2) oxidation state
$Fe \rightarrow Fe^{3+} + 3e^{\ominus}$ Fe^{3+} — (+3) oxidation state

$Cl^- + e^{\ominus} \rightarrow Cl$ Cl^- — (-1) oxidation state

Metals — (+ve) oxidation state
Non metals - At least one common (-ve) oxidation state.
d-block elements - Widest range of oxidation states.
Atoms of same element with diff. oxidation states can have different properties like colour.

Fe^{2+} - Green, Fe^{3+} - Brown Cu^{2+} - ~~Green~~ Blue, Ni^{2+} - Green

Exception - $Zn^{2+}(3d^{10})$ $Cd^{2+}(4d^{10})$ $Hg^{2+}(5d^{10})$ — colourless (Because s and p-block elements — colourless)

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colour may arise when very high polarising power electro(+ve) ion binds with anions.

$[CrO_4]^{2-}$ $[MnO_4]^-$ $[Cr_2O_7]^{2-}$ Ag(I) PO_4^{3-} PF_3

Elements with highest oxid^n state — oxidising agents
——" —— lower ——" —— — Reducing agents

Fe^{3+}, Mn^{4+}, Cr^{6+}, Mn^{7+}, Sn^{4+} — oxidising agents

+6, -2 $Na_2S_2O_3$

Fe^{2+}, Mn^{2+}, Cr^{3+}, Sn^{2+} — Reducing agents

Cl^- NH_2^- SO_4^{2-} NO_2^- - Nitrate $Fe_3O_4(Fe^{3+}, Fe^{2+})$
CN^- O^{2-} oxo OH^- $Fe_2O_3(Fe^{3+})$
NO_2^- Nitrite O_2^{2-} peroxo SO_3^{2-}
CO_3^{2-} $C_2O_4^{2-}$ NH_4^+

ZnH_4 CS_2
$Na[AuCN_2]$ $Na_3Co(NO_2)_6$
BaO_2 — Peroxide NaCl
$(NH_4)_2MoO_4$ FeO■ $Fe_2(SO_4)_3$

Rules

1) Pure metal are all zero.
2) F is +
3) Metals 1A - (+1), 2A - (+2)
4) H - (+1) with metal (-1)
5) O is usually (-2)
6) Halogen —" — (-1)

Inert-Pair effect: Heavier elements of group 13 to 17 often have oxid^n states lower by 2 than max. predicted for gr. i.e. Tl - (+1) oxid^n state rather (+3) because of Increasing Ionization energies & decreasing bond strength down the group.

B	$[He]\,2s^2 2p^1$	801	4S, 5S, 6S e$^\ominus$ are not well shielded from nucleus by d & f orbitals thus large EN charged high IE.
Al	$[Ne]\,3s^2 3p^1$	578	
Tl	$[Xe]\,4f^{14} 5d^{10} 6s^2 6p^1$	589	

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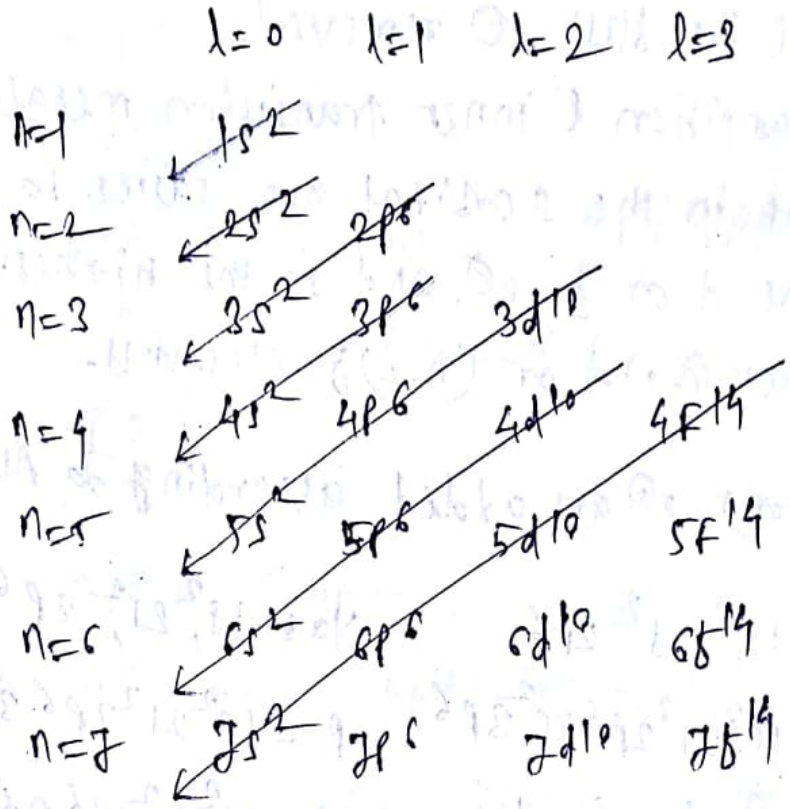
Modelung's rule :-



The energy of the 3d orbital has been mathematicall shown to be lower than that of 4s orbital, electro occupy the 4s orbital first before the 3d orbital.
3d electrons are more likely to be found closer to the nucleus hence they repel each other more strongly

The electronic conf. of cations is assigned by removin electrons first in the outermost p orbital, followe by the s orbital & finally the d orbitals (if any more electrons need to be removed).

$_{20}Ca^{2+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6$

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For main group elements, the e⊖ that were added last are the first e⊖ removed.
For transition & inner transition metals, however electrons in the s orbital are easier to remove than the d or f e⊖. and so the highest n.l e⊖ are lost, then (n-1) d or (n-2) f electrons.

For anions e⊖ are added according to Aufbau principle.

$Na^+ - 1s^2 2s^2 2p^6$ $Na = 1s^2, 2s^2, 2p^6, 3s^1$

$P^{3-} - 1s^2 2s^2 2p^6 3s^2 3p^6$ $P = 1s^2 2s^2 2p^6 3s^2 3p^3$

$Al^{3+} - 1s^2 2s^2 2p^6 3s^1$ $Al = 1s^2 2s^2 2p^6 3s^2 3p^1$

$Fe^{2+} - 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ $Fe = 1s^2, 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

$Sm^{3+} = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$

$Sm = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$

Applications of Slater rules :-

1) Zeff for 2p e⊖ in nitrogen - $(1s^2)(2s^2 2p^3)$

$Z_{eff} = Z - [(0.35 \times 4) + (0.85 \times 2)]$

$= 7 - 3.10$

$= 3.90$

2) Zeff for 3p electron in Silicon - $(1s^2)(2s^2 2p^6)(3s^2 3p^2)$

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$Z_{eff} = Z - [(0.35 \times 3) + (0.85 \times 8) + (1.00 \times 2)]$

$= 14 - 9.85$

$= 4.15$

3) Z_{eff} for 2p e⊖ in fluorine $= (1s^2)(2s^2 2p^5)$

$Z_{eff} = Z - [(0.35 \times 6) + (0.85 \times 2)]$

$= 9 - [3.8]$

$= 5.2$

4) Z_{eff} for 6e⊖ in platinum $= (1s^2)(2s^2 2p^6)(3s^2 3p^6)(3d^{10})(4s^2 4p^6)(4d^{10})(4f^{14})(5s^2 5p^6)(5d^8)(6s^2)$

$Z_{eff} = 78 - [(0.35 \times 1) + (0.85 \times 10) + (1.00 \times 60)]$

$= 78 - [73.95]$

$= 4.15$

8) Z_{eff} for 3d e⊖ in zinc $= (1s^2)(2s^2 2p^6)(3s^2 3p^6)(3d^{10})(4s^2)$

$Z_{eff} = Z - [(0.35 \times 9) + (1.00 \times 18)]$

$= 30 - 21.15 = 8.85$

4s e⊖ in zinc

$Z_{eff} = Z - [(0.35 \times 1) + (0.85 \times 18) + (1 \times 10)$

$= 30 - 25.65$

$= 4.35$

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Acids and Bases

Chemical substances are classified as acids, bases & salts by Robert Boyle.

* Acid – Acidus - means sour (i.e. sour in taste)

i) Substance when added to water produces H^+ ions.
ii) Concentration of H^+ ions in solution determine its strength of an acid. more H^+ — stronger acid
iii) Turns blue litmus red, pH < 7 e.g. CH_3COOH, HCl, H_2SO_4

* Base –

i) Substance which when added to water produces OH^- ions.
ii) Bitter in taste.
iii) Red litmus turns blue, pH > 7 e.g. NaOH, NH_3 etc.

Theories of Acids and Base :-

A) Arrhenius theory (1887)

i) It is based on electrolyte dissociation in aq. soln.
ii) Acid produces H^+ ions $HCl \rightarrow H^+ + Cl^-$
iii) Base produces OH^- ions $NaOH \rightarrow Na^+ + OH^-$
iv) Neutralisation rea^n $HCl + NaOH \rightarrow NaCl + H_2O$
v) Limitations – 1) Limited to aq. soln only,
2) Could not explain acidic nature of CO_2, SO_2, Cl_2O, N_2O etc.
3) Could not explain the basic nature of NH_3, CaO, ~~H_2O~~ Na_2O etc.

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B) Bronsted-Lowry theory :- (1923)

i) Based on proton transfer, also called Protonic theory.

ii) Bronsted acid – substance that donates proton.

iii) Bronsted-Lowry acid is a proton donor

$HCl \longrightarrow H^+ + Cl^-$ tendency to lose or donate proton.

iv) The substance that accepts a proton is Bronsted base.

v) Shows tendency to gain a proton is bronsted base i.e. proton acceptor

$NH_3 + H^+ \longrightarrow NH_4^+$

v) Transfer from acid proton to base is called neutralizn

$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

Conjugate acid-base pairs :-

i) A pair of acid-base which differs by a single proton is known as conjugate acid-base pair.

ii) The removal of proton from a bronsted acid gives its conjugate base.

$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

Bronsted acid — conjugate base

iii) The addition of a proton to a bronsted base gives its conjugate acid.

$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$

base proton conjugate acid

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Conjugate base of strong acid is weak base.

HCl – strong acid

Cl^- – weak base (conjugate)

Conjugate base of weak acid is strong base.

CH_3COOH – weak acid

CH_3COO^- – strong base (conjugate)

Conjugate acid of strong base is weak acid.

OH^- – strong base

H_2O – weak acid (conjugate)

Conjugate acid of weak base is strong acid.

C_2H_5OH – weak base

$C_2H_5\overset{\oplus}{O}H_2$ – strong acid (conjugate)

<u>According to Bronsted-Lowry theory</u>,

Greater tendency to donate proton – strong acid

e.g. H_2SO_4, HNO_3

Less tendency to donate proton – weak acid

e.g. CH_3COOH, H_2S

Greater tendency to accept proton – Strong Base

e.g. $CH_3COO^{\ominus}$, OH^-

Less tendency to accept proton – weak base

e.g. Cl^-

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Amphiprotic substance

Substance which shows tendency to donate or accept protons is called amphiprotic substance.

(acid) $H_2O \longrightarrow H^+ + OH^-$ (conjugate base)

(Base) $H_2O + H^+ \rightarrow H_3O^+$ (conjugate acid)

Leveling effect of water :

In water all the strong acids like $HClO_4$, HCl produce equal concentration of H^+ ions since they are 100% ionized in water. Similarly in case of strong bases. This is known as leveling effect of water.

Limitations

i) Proton acceptance or donation only happen in the presence of another substance.

ii) Could not explain acidic nature of electron deficient compounds like $AlCl_3$, BCl_3 etc.

c) Lewis theory : (1923)

i) Based on tendency to transfer electron pair, therefore it is called electronic theory.

ii) The substance that can accept a pair of electron to form a co-ordinate covalent bond is called as Lewis acid. Lewis acids are electron pair acceptors.

e.g. BCl_3, $AlCl_3$, CH_3^+ etc.

iii) Substance which donates $e^\ominus$ pair called Lewis base.

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e.g. NH_3, H_2O, Cl^- etc.

Neutralization - transfer of e⊖ pair from donor to acceptor is called neutralization, forms co-ordinate covalent bond.

$$BF_3 + :NH_3 \longrightarrow (BF_3 \leftarrow NH_3)$$

iii) Lewis acids are electrophiles i.e. e⊖ loving or seeking
Lewis bases are nucleophiles i.e. Nucleus rich or seeking

iv) Lewis acids contain vacant orbital.
Lewis base contains lone pair of electrons.

Lewis acids	Lewis bases
All cations are Lewis acids since they are able to accept e⊖. Ex. Cu^{+}, Fe^{+}, Fe^{3+}	most Lewis bases are anions e.g Cl^-, OH^- NH_2^-
Lewis acids are compounds with incomplete octet. e.g. BCl_3, $AlCl_3$	Lewis base are molecules with two lone pair of e⊖ on central atom. e.g. NH_3, H_2O
Compounds with double bonds other than C=C e.g. SO_2, CO_2	Compounds with C=C, C≡C, multiple bonds e.g. C_2H_4, C_2H_2
molecules in which central atom can expand its octet with vacant d-orbitals present in its valence shell. e.g. SiF_4, $SiCl_4$	

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Limitations of Lewis theory :-

i) According to Lewis theory, neutralization reaction occur very slowly. But in fact, the acid base neutralization reaction occur quickly.

ii) Could not explain the strength of acids & base.

iii) Could not explain catalytic activity of H^+ ion.

iv) All the acid base reactions do not involve formation of co-ordinate covalent bond.

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

* Acid-base properties in periodic table :-

Hydrides — compounds formed bem H & other elements

In a period, — more basic hydride ⟶ more acidic hydride

NaH ⟶ HCl

$$NaH + H_2O \rightarrow Na^+ + H_2 + OH^-$$

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

In a column, acidity increases with ~~decrease~~ decrease in EN.

CH_4	NH_3	H_2O	HF	Increase in acidic strength
Neutral	weak base	.....	weak acid	
SiH_4	PH_3	H_2S	HCl	
Neutral	weak base	weak acid	strong acid weak conj. base	

Stronger acids — weaker & more polar H-X bonds.
Greater size of anion, less nuclear attr.

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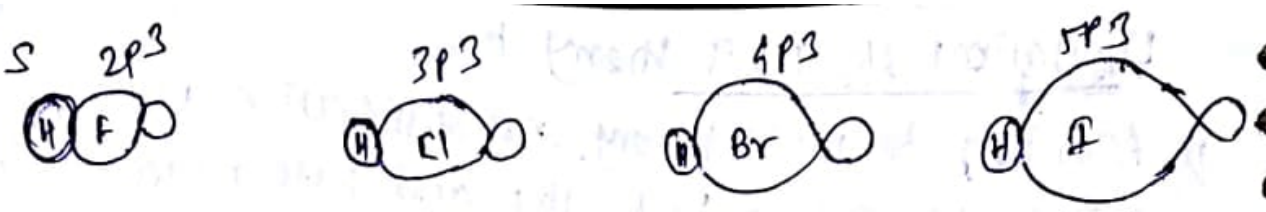

HF HCl HBr HI

orbital overlap bern is of p orbitals of halogens decreases as size increases down the group, hence the bond is less strong & it is a better acid. I⁻ conjugate base more stable bcoz charge is spread out.

Acidity increases across period because increasing EN thus stronger acid (more ionic compound H+ x⁻ compel dissociation more feasible) However down the gr. total bond strength becomes much weaker, ~~because~~

H-F – 135 Kcal/mol Decreasing bond energy
H-Cl – 103 Kcal/mol increase the tendency to
H-Br – 88 Kcal/mol HX to split up into H+ & X⁻
H-I – 71 Kcal/mol ion in aq. soln.

<u>Oxyacids</u> – H_nYO_m e.g. H_2CO_3, H_3PO_4, HNO_3

$$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$

H–O–I H–O–Br H–O–Cl increase in acid strength

EN 2.5 2.8 3 →

No. of oxygen atoms on central atom increases

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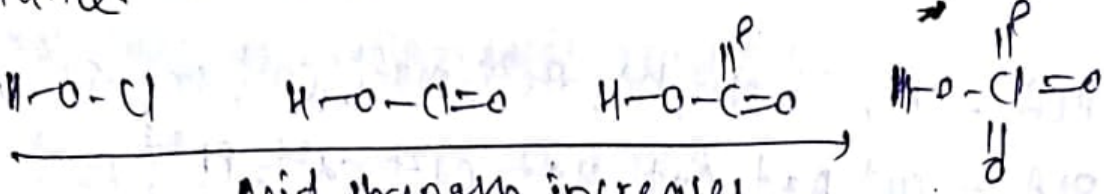
acidity increases because charge is stabilized by the resonance.



HCl, HBr, HI, H_2SO_4, HNO_3, $HClO_3$, $HClO_4$ — Strong acids

LiOH, NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$ — Strong Bases

* HSAB Theory :- Ralph Pearson (1960)

Stability of metal complexes & mechanisms of their reactions.

HOMO / LUMO interaction.

Hard Lewis acids - small ionic radii, high positive charge, empty orbitals in the valence shell & high energy LUMOs.

Soft Lewis acids - Large ionic radii, low positive charge, completely filled at. orbitals & low energy LUMOs.

Hard Lewis bases - small ionic radii, highly electronegative, weakly polarizable & high energy HOMOs.

Soft Lewis bases - Large ionic radii, intermediate EN, highly polarizable & low energy HOMO's.

In short, Hard acids & bases — small & Non-polarizable
soft acids & bases - Larger & more polarizable

HSAB concept says, hard acids prefer binding to the hard bases to give ionic complexes, whereas soft acids prefer binding to soft bases to give covalent complexes.

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Hard acid – soft base
soft acid – Hard base } covalent, more reactive or less stable (NaH, $LiAlH_4$, CH_3Li, $Pb(OAc)_4$)

HLA – H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Si^{4+}, Al^{3+}

SLA – Cu^+, Ag^+, Au^+, Hg^+, Pd^{2+}, Cd^{2+}, Pt^{2+}, As^{3+}

HLB – H_2O, OH^-, F^-, [illegible], SO_4^{2-}, CO_3^{2-}, ClO_4^-, RO^-, NH_3, PO_4^{3-}

SLB – S^{2-}, $RS^{\ominus}$, I^-, CN^-, SCN^-, R^-, H^-, P, S, Cl^-

Applications of HSAB principle :-

i) H-Bonding – Strong H-bonding is possible in case of H_2O, NH_3, HF since donor (N, O, F) are hard lewis bases interacts with Hard acid H are stronger.

ii) Linkage of Ambidentate ligands to metal atoms –

SCN^- — M–SCN – thiocyanate
M–NCS – Isothiocyanate

Choice of binding is decided by soft or hard acid base behavior. S comparatively soft than N atom. hence soft metal ions are S-bound while hard metal ions are N-bound.

$[Pt^{2+}-SCN]^+$, $[Cr^{3+}-NCS]^{2+}$

Fe^{2+} reacts with SCN^- — $[Fe(SCN)]^+$ bright red — Border line acid

Cr^{3+} — " — $[Cr(SCN)]^{2+}$ — Hard acid – N

Symbiotic effect :- Hard-soft character of metal ion is altered by other groups attached.

Co^{3+} – Hard acid in $[Co(NH_3)(NCS)]^{3-}$ Co — NCS

when $[Co(CN)_5]^{2-} + SCN \longrightarrow [Co(CN)_5(SCN)]^{3-}$ Co–SCN

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Hardness of Co^{3+} is reduced due to 5 soft base ligand (CN^-) thus $[Co(CN)_5]^{2-}$ behaves as soft acid.

iii) Predict direction of Inorganic reactions :-

$$AsF_3 + PI_3 \longrightarrow AsI_3 + PF_3$$

As^{3+}, P^{3+} — soft but As^{3+} is more softer due to larger size. I^- softer than F^- thus reaction proceeds to right.

$$2PF_2I + 2Hg \longrightarrow Hg_2I_2 + P_2F_4$$

P_2F_4 is prepared by treating PF_2I with Hg where iodine rather than F removed by Hg. Hg^+ is soft acid prefers soft base I^- rather than hard base F^-.

iv) Solubility in water :-

compound formed due to soft acid-base combination is more covalent & less soluble in polar solvents like water. AgF — insoluble in water Ag^+, I^- — soft
LiF — soluble in water Li^+ - Hard acid
(Polar covalent) I^- — soft base

v) Precipitation reactions of qualitative analysis :-

Ag^+, Hg^+, Hg^{2+} & borderline acids — Fe^{2+}, Ni^{2+}, Cu^+, Zn^{2+}
precipitated as sulfides —— soft — soft interaction

HCl — precipitates AgCl, $PbCl_2$, Hg_2Cl_2 — soft

$(NH_4)_2CO_3$ — $CaCO_3$, $SrCO_3$, $BaCO_3$ — Hard

vi) Nucleophilic addition of α,β-unsat carbonyl comp.

α of α,β — Co-carbon — Hard electrophilic center
β — β-carbon — soft —"—

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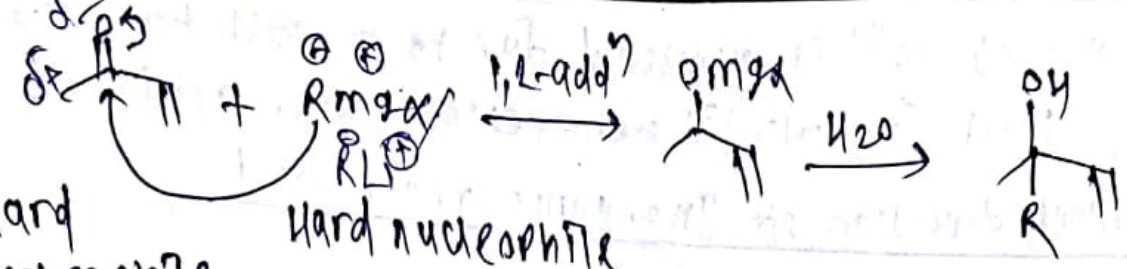

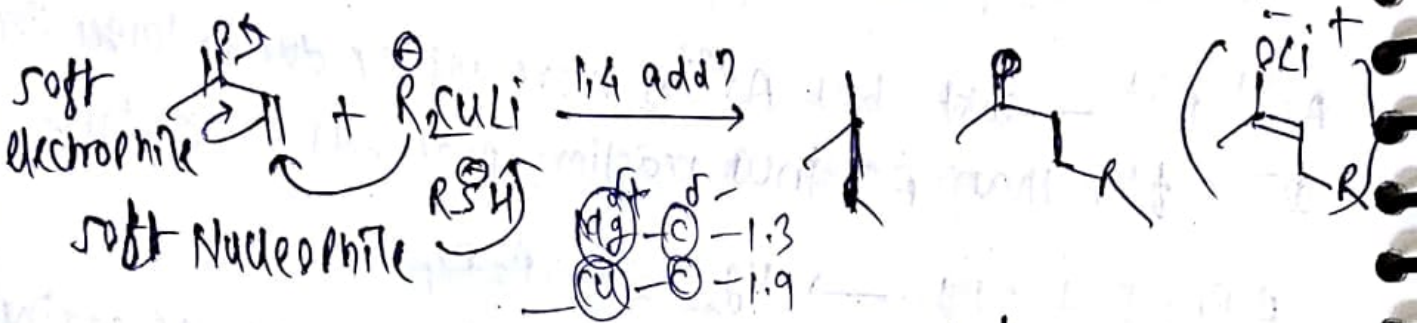

* Drawbacks of Pearson's HSAB model :-

i) Direct contradiction with Fajan's rule.
e.g. BeF_2 — more covalent nature (Fajan's) - Beck
BeF_2 — hard acid expected to show charge controlled bonding results more ionic compounds. (HSAB principle)
but that is not true.

ii) Since H^+ as hard acid & H^- as soft base, according to HSAB interaction betn them must be polar covalent & H_2 must be unstable indeed H_2 is more stable molecule with pure covalent nature.

* Hybridization :- HA-HB – ionic (charge controlled bond)
SA-SB – covalent (FMO controlled complex)

The mixing of atomic orbitals to form equivalent orbitals is hybridization & the resulting orbitals are called hybrid orbitals. (same energy)
e.g. CH_4 molecule, 4 eqv. orbitals with unpaired e⊖ of carbon atom are involved in bonding with 4 s

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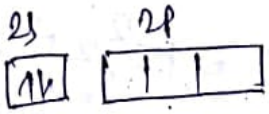
orbitals of H atoms, avoid mutual repulsion forms tetrahedral geometry with bond angle 109.5°. Similarly bond angles in NH_3 and H_2O molecules can be explained.

Theory and Energetics of Hybridization :-

Pure atomic orbitals having similar energy combine & form equivalent orbitals i.e. hybridization.

e.g. BeF_2

$Be = 1s^2 2s^2$

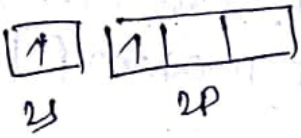
Be = 

Valence electrons $2s^2$.

G.S

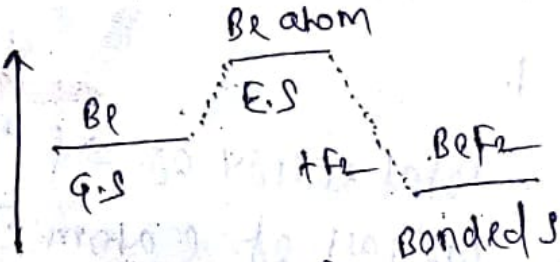
In GS, Be having no unpaired electrons — zerovalent

BeF_2 — covalency 2

Be = 

E.S 2s 2p

Two half filled orbitals forms 2 covalent bonds with F_2. BeF_2 energy level is stable than Be E.S. thus formation of BeF_2 is energetically feasible.

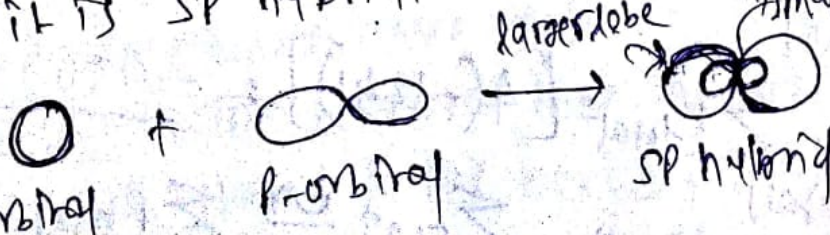


BeF_2 =

Electrons gained by bonding with F atoms

The 2s & 2p orbitals have diff. energies & hence two covalent bonds have to be of different strength.

In E.S of Be, one s & one p orbital each having unpaired e⊖, mix, combine & form two new orbitals of equal energy thus it is sp hybridization & resulting sp hybrid orbitals



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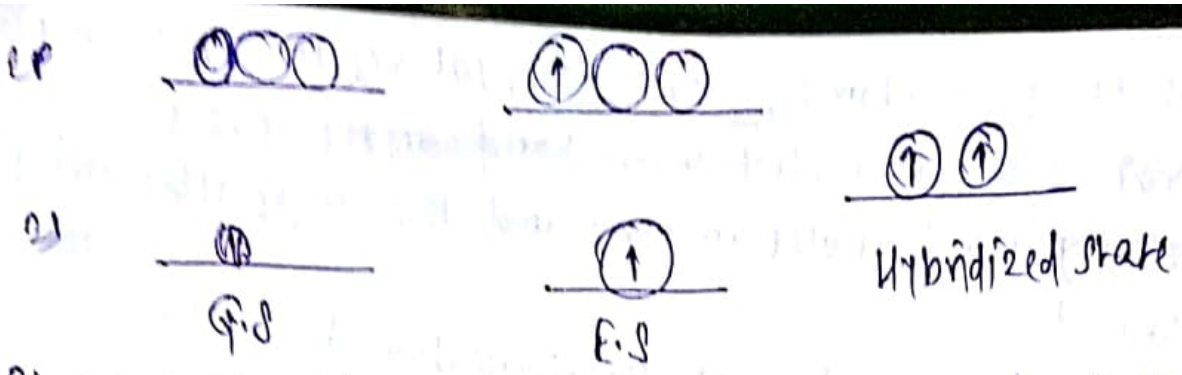


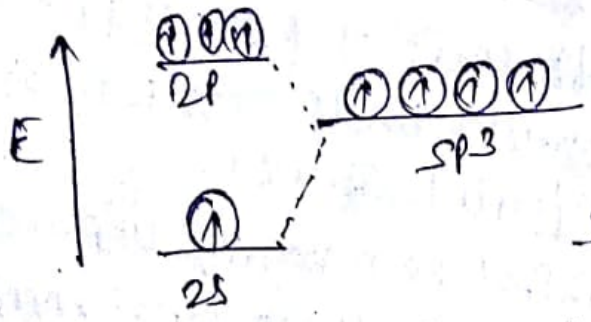
Since hybrid orbitals have lower energy & have larger directed lobes, they overlap more effectively & form stronger bonds than pure atomic orbitals.

CH_4 Molecule :- $C = 1s^2, 2s^2 2p^2$

one s & 3p orbitals hybridize (sp^3 hybridization) and four equivalent hybrid orbitals are formed. Each hybrid orbital effectively overlaps with s orbital of H atom & forms four equivalent C-H bonds.

Energetics of Hybridization :-

2S – −1878 kJ/mol
2P – −1028 kJ/mol



Total energy of s & three p orbitals of C atom is

$$\sum E_{s+p^3} = [-1878 + 3(-1028)]$$
$$= -4962 \text{ kJ/mol}$$

$$\therefore E_{sp^3} = \frac{1}{4}[E_s + 3E_p]$$
$$= \frac{1}{4}[(-1878 + 3(-1028)]$$
$$= -1241 \text{ kJ/mol}$$

∴ Energy of each sp^3 hybrid orbital with one electron $= -1241$ kJ/mol

∴ Total energy of 4 hybrid orbitals $= \sum E_{total} = [4(-1241)] = \underline{-4964 \text{ kJ/mol}}$

$$\therefore \sum_{s+p^3} \simeq \sum E_{total}$$

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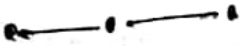
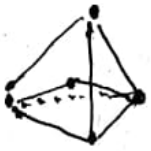
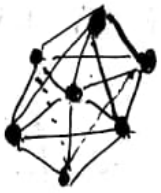
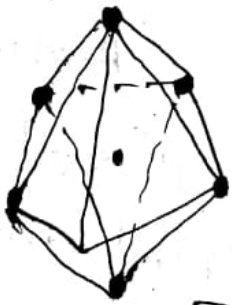
∴ sp^3 hybridization in C atom will not cost extra energy & hence is favored. The four bonds in CH_4 are at four corners of tetrahedron making bond ~~distance~~ 109.5° angle. The energetics of hybridization together with the principle of good overlap are important in determining structure of many molecules.

No. of e⊖ in outer shell	Shape of Molecule	Bond Angles
2	Linear 	180°
3	Trigonal planar	120°
4	Tetrahedron 	109.5°
5	Trigonal bipyramid	120° & 90°
6	Octahedron 	90°
7	Pentagonal bipyramid 	72° and 90°

Covalent bond is directional unlike ionic bond, therefor covalent molecules have definite shapes.
Sidgwick-Powell suggested that the shape of a covalent molecule is related to the no. of e⊖ in the valence in th valence shell of the central atom.

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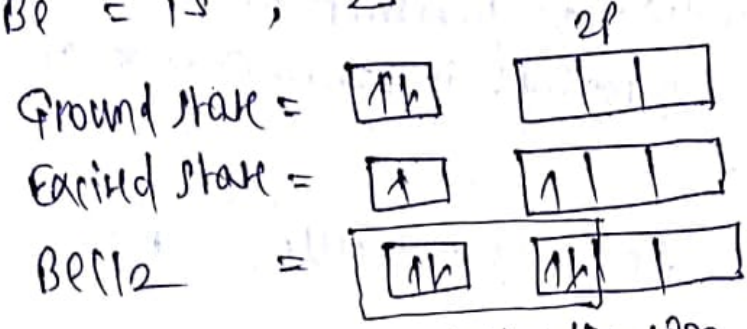
Different types of hybridization :

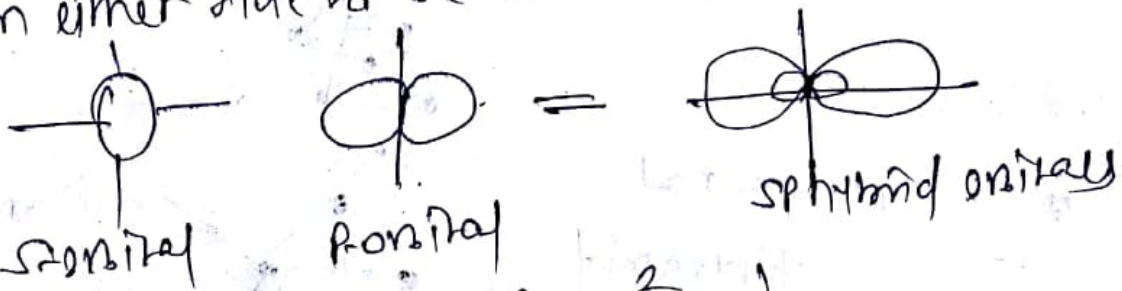
sp hybridization -

Be = $1s^2$, $2s^2$



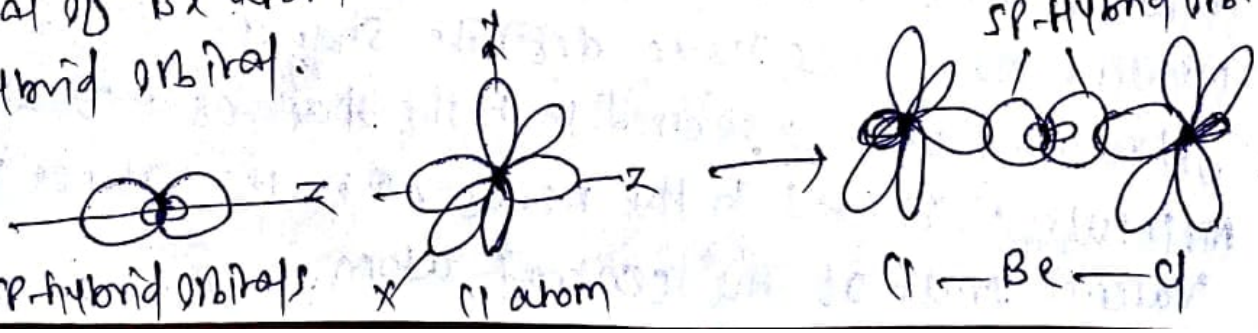
sp hybridization

In $BeCl_2$ molecule, when Cl atom approaches Be atom to form covalent bonds, there is release of energy which promotes one of 2s e⊖ into empty 2p orbital. Half filled 2s & 2p orbitals hybridize & form two identical sp hybrid orbitals. Each hybrid orbital contains one e⊖ & has a large lobe and a small lobe. Large lobe is bigger than p orbital lobes thus greater overlap with Cl atom orbital. To minimize repulsion between the electrons, two sp orbitals (hybrid) lie in a straight line on either side of Be atom with bond angle 180°.



Cl = $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$

Half filled p-orbital overlaps with one of half filled sp hybrid orbital of Be atom. Second Cl atom also overlaps second sp hybrid orbital.



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sp2 hybridization — BF_3 molecule

sp3 hybridization — $SiCl_4$ molecule

*Shape of molecules - The geometry of a molecule depends on the arrangement of orbitals around the central atom and the bond angles they make with one another in space around the central atom.

VSEPR theory :

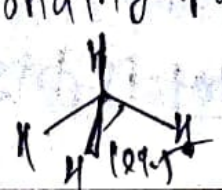
For maximum stability of a molecule, the orbitals occupied by electrons (bonding & non bonding) in the valence shell of the central atom should be so arranged in space that they lie as far away from one another as possible to have minimum repulsion.

Structure of molecules containing lone pairs of electrons

If central atom in molecule has lone pair of e⊖, then the geometry of molecule get distorted due to changes in the bond angles, due to repulsion bet lone pair e⊖ & other e⊖. Bonding pair e⊖ are attracted by two nuclei whereas lone pair e⊖ are attracted by own nuclei thus electron cloud spreads and occupy larger angular volume and affects other e⊖ pairs changes bond angles.

Lone pair effect - The distortion in the structure of molecule due to presence of lone pairs is called lone pair effect.

Lone pair - lone pair repulsion > Lone pair - Bonding pair > Bonding pair - Bonding pair repulsion.



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the no. of lone pairs increases the extent of distortion increases & bond angles get reduced.

* Application of VSEPR theory to determine molecular structure :-

1) NH_3 – sp^3 hybridization

$_7N = 1s^2 2s^2 2p^3$

G.S =

NH_3 =

sp^3 hybridization

In NH_3 molecule, there are 8 e⊖ (4 e⊖ pairs) in valence shell of N atom. Five of N & 3 of H atoms. The expected geometry is tetrahedron with 109.5°. But of 4 e⊖ pair, 3 are bonding pairs & 1 is lone pair. Single lone pair distorts bond angle slightly from 109.5° to 107°. Due to lone pair effect, structure of NH_3 is distorted & has pyramidal structure.

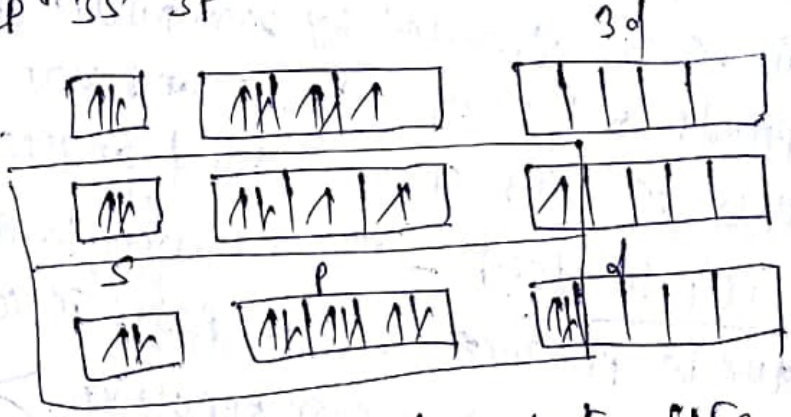
2) ClF_3 molecule – Chlorine trifluoride – sp^3d hybrid

$_{17}Cl = 1s^2 2s^2 2p^6 3s^2 3p^5$

G.S =

E.S =

ClF_3 =



total 10 e⊖, out of 7 of Cl & one of each F. ClF_3, 5 e⊖ pairs in valence shell of Cl atom. 3 are bonding & 2 are lone pairs. Expected geometry is trigonal

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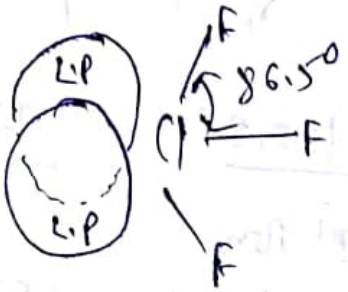
bipyramidal with lone pairs at equatorial position. Due to lone pair repulsions, axial Cl-F bonds bend slightly away from lone pairs. Hence molecule has "bent T" structure with bond angle less than 90° i.e. 86.5°



3) **BrF_5 molecule** – Boron ~~[illegible]~~ pentafluoride [TeF_5]

sp^3d^2 hybridization — expected octahedral but actual geometry square pyramid

4) **PX_3 molecule** :- Phosphorus trihalides

Central P atom is assumed to undergo sp^3 hybridization.

$_{15}P = 2, 8, 5$

	3s	3p		
G.S =	↑↓	↑	↑	↑
PX_3 =	↑↓	↑↓	↑↓	↑↓

sp^3 hybridization

In PX_3, valence shell of P atom, there are 8 e⊖ (five of P & one of each X) & expected geometry is tetrahedral with bond angle 109.5°. Out of these 8 e⊖ or 4 e⊖ pairs, three are bonding pairs & one is lone pair. The expansion of this lone pair distorts structure & bond angle is reduced. The reduction in bond angle in PX_3 depends on EN of X.

PF_3 — F highly EN, bonding pair attracted more toward F atoms. They move away from P nucleus allowing maximum expansion of lone pair. Thus bond angle in PF_3 — 97.8°

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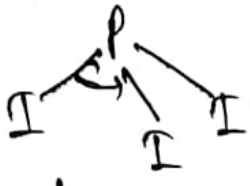
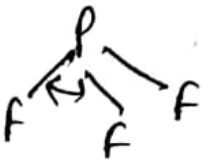
from Fluorine to Iodine, decreasing EN causes less attraction for bonding e⊖. This result increasing bond angles than PF_3 do PI_3.



$102°$

$101.5°$

$100.3°$

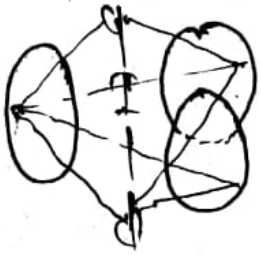


$97.8°$

5) $[ICl_2]^-$ — Dichloroiodate(I) ion

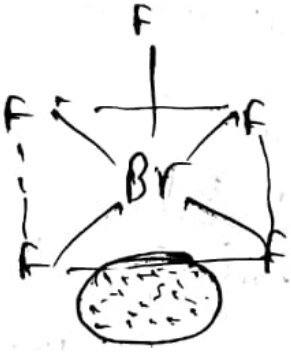
sp^3d hybridization — Expected trigonal bipyramidal

Actual - linear



$180°$

$[TeF_5]^-$



BrF_5

$104.5°$

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