INORGANIC CHEMISTRY

ATOMIC STRUCTURE AND BONDING

1896 : Becquerel → Radioactivity of U
1897 : J.J. Thompson → e have -ve charge
1909 : R.A. Millikan → e^- is charge and mass
1911 : Rutherford → Established the simplest atomic model
1913 : Bohr → Bohr's Theorem
1913 : Moseley → Atomic no.

Drawbacks of Rutherford's model:

1) By gradual emission of E, 'e' moves towards the nucleus & finally combines with it. So all the atoms will be unstable

2) For cont. radiation of energy by the rotating e^- conti. spectrum is expected but we get a disc. spectrum.

Bohr's theory:

- K, L, M, N orbits

1) e^- orbits are those who have an ang. mom of $\frac{nh}{2\pi}$

2) Stationary orbit concept. [e^- do not radiate energy while rotating is those orbits]

3) e^- emits / absorbs energy on jumping from one orbit to another.

'E' is emitted when e^- moves from one stationary orbit of higher energy to one stationary orbit of lower energy.

$E_2 - E_1 \propto \nu$ [freq. of emitted radiation]

$$\frac{mv^2}{r} = \frac{ze^2}{4\pi\varepsilon_0 r^2}$$ [ε_0 → permittivity of vaccum]

$$v^2 = \frac{ze^2}{4\pi\varepsilon_0 mr} \rightarrow (1)$$

$$mvr = \frac{nh}{2\pi} \rightarrow (2)$$

$$\frac{n^2h^2}{m^2r^2 4\pi^2} = \frac{ze^2}{4\pi\varepsilon_0 m r}$$

$$\boxed{r = \frac{n^2h^2\varepsilon_0}{\pi z m e^2}}$$

$$E_{kinetic} = \frac{1}{2} \times m \times v^2 = \frac{1}{2} \times \cancel{m} \times \frac{ze^2}{4\pi\varepsilon_0 \cancel{m} r} = \frac{ze^2}{2 \times 4\pi\varepsilon_0 r}$$

$$E_K = \frac{ze^2 \cancel{\pi} z m e^2}{8\cancel{\pi}\varepsilon_0 n^2h^2\varepsilon_0} = \frac{z^2 m e^4}{n^2 8\varepsilon_0^2 h^2}$$

$E_{potential}$ → work done in bringing the e^- from inf to its position of n^{th} Bohr orbit

$$E_p = \int_{\infty}^{r} \frac{ze^2}{4\pi\varepsilon_0 r^2} dr = \frac{-ze^2}{4\pi\varepsilon_0 r}$$

Total energy : $E_k + E_p = \frac{ze^2}{8\pi\varepsilon_0 r} - \frac{ze^2}{4\pi\varepsilon_0 r}$

$$= \frac{-ze^2}{8\pi\varepsilon_0 r}$$

$$\boxed{\text{Total energy} = \frac{-mz^2e^4}{8\varepsilon_0^2 n^2 h^2}}$$

$T.E = -K.E \qquad 2K.E = -P.E$

Explanation of H spectrum by Bohr :

$$\frac{1}{\lambda} = \bar{\nu} = \frac{me^4 z^2}{8\varepsilon_0^2 c h^3} z^2 \left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right]$$

$$= RZ^2 \left[\frac{1}{n_f^2} - \frac{1}{n_f^2}\right]$$

R → Rydberg's constant

n_f	n_i		
1	2, 3, 4 ..	Lyman.	UV
2	3, 4, 5 ..	Balmer	Visible
3	4, 5, 6 ..	Paschen	IR
4	5, 6, 7 ..	Brackett	IR
5	6, 7, 8 ..	Pfund.	IR
6	7, 8, 9 ..	Humphrey.	IR

H- Spectrum is a discrete spectrum.
[fine-line spectrum]

Only 1 e^- is there, which jumps ?

* Zeeman & Stark effect (couldn't exp. by Bohr's theory)
→ Splitting of a spectrum line into several comp. with appl. of magnetic field — Zeeman; electric field — Stark

Acc. to Bohr's theory, Nucleus remains stationary expect for rotation on its own axis.

⇓

This is true only if the mass of nucleus is ∞, which is not true.

Hence, Nucleus is always vibrating about the centre of gravity.

∴ Mass of e^- is reduced.

Reduced mass $(\mu) = \frac{Mm}{M+m}$

M → mass of nucleus
m → mass of electrons.

∴ Rydberg's constant, $R = \frac{e^4}{8\epsilon_0^2 c h^3}\left(\frac{Mm}{M+m}\right)$

Quantum numbers: The minimum characteristics by which an e^- can be completely identified in an atom are called Quantum numbers.

i) Principal (n)
ii) Azimuthal (l) [Subsidary quan. no]
iii) Magnetic (m)
iv) Spin (s)

i) n gives us a view about energy and size of the e^- orbit.

	K	L	M	N	
n :	1	2	3	4	....

[Bohr] circular orbits

ii) l gives us a view about shape of the e^- orbit.
[Sommerfield] → some of the orbits are elliptical

The shape of ellipse : $\frac{\text{Length of major axis}}{\text{Length of minor axis}} = \frac{n}{k}$

where, k = 1, 2, 3 ... n (azimuthal quan. no)

For n = 4, $\frac{4}{1}, \frac{4}{2}, \frac{4}{3}$ are elliptical orbits

$\frac{4}{4}$ → circular orbit.

Later they were modified as,
l = 0 → s orbital
l = 1 → p orbital
l = 2 → d orbital
⋮

l varies from 0 to n-1

iii) m → orientation of e^- in the orbit w.r. to an external magnetic field.
[dinde] ranges from $-l$ to $+l$.

iv) s → spin of the e^- in an orbital
$+1/2$ → clockwise
$-1/2$ → anti-clockwise
[Samuel Goudsmit]

e^- having $+1/2$ spin slightly have more energy than those with $-1/2$ spin.

Building up of elec. config of an atom:
i) Auf-bau's principle
ii) Pauli's exclusion principle
iii) Hund's rule.

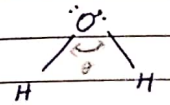
i) Auf-Bau principle:
Auf-bau - German word for 'building up' or 'construction'
Orbitals are filled with e^- in order of their increasing energy. Orbitals of lowest energy will be filled up first. [$n+l$ values]
For same $n+l$ value, lower n value will have lower energy.

ii) Pauli's exclusion principle:
No two e^- of an atom can have same set of quantum numbers.

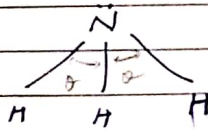
iii) Hund's rule of max. multiplicity:
e^- into e^- enter into the degenerate atomic orbitals in such a way that they contain max. no of unpaired electrons with their spins parallel.

CHEMICAL BONDING

A covalent bond is the bond established b/w two atoms by the overlap of their atomic orbitals each containing one unpaired e^- of opposite spin. They are directional in nature.



θ, expected - 90° (2p_x & 2p_y are mutually ⊥)
observed - 104°



θ, Expected - 90°
Observed - 107.3°

Final geometry is determined by,
1) Hybridisation
2) Mutual repulsion of bonding e^- cloud.
3) Influence of unshared e^- on bonding e^-

Unpairing & promotion of e^- prior to bond formation:

Consider Be.

GS - $\boxed{1L}$ $\boxed{1L}$ $\boxed{\ \ }$ $\boxed{\ \ }$ $\boxed{\ \ }$
1s 2s 2p

ES - $\boxed{1}$ $\boxed{1}$ $\boxed{\ \ }$ $\boxed{\ \ }$ $\boxed{\ \ }$ 2 unpaired e^- ↓ 2 bonds.
2s 2p

H — Be — H

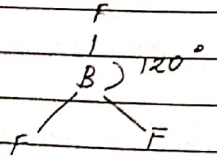
E_{req} to unpair e^- < E_{rel} is bond formation.

* Without considering hyb. in CH_4, C-H bond lengths are not equal.

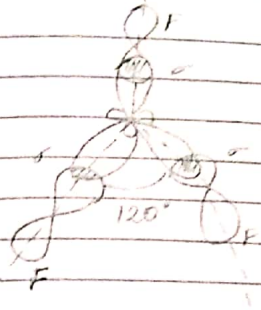
sp^2 hybridization:

BF_3

	2s	2p	
B (GS) →	$\boxed{1L}$	$\boxed{1}$ $\boxed{\ \ }$ $\boxed{\ \ }$	
B (ES) →	$\boxed{1}$	$\boxed{1}$ $\boxed{1}$ $\boxed{\ \ }$	→ sp^2 orbital
BF_3	$\boxed{1L}$	$\boxed{1L}$ $\boxed{1L}$ $\boxed{\ \ }$	
	↑ F	↑ F ↑ F	

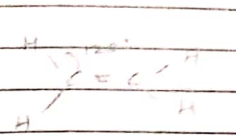


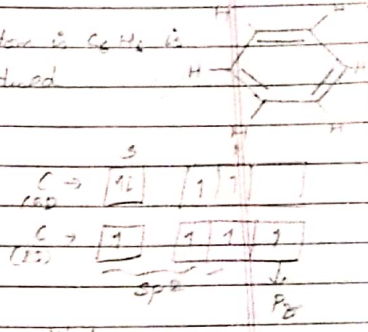
overlap of 3 sp^2 hyb. orbitals of B with 3 2p orbitals of 3F atoms to form 3 σ bonds.



sp^2 hybridisation.

∴ Each C atom in C_2H_4 is sp^2 hybridised



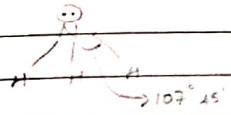


P orbital overlap to form π - bonds

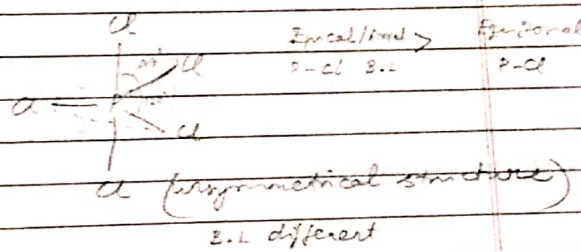
No diff. in B.L due to delocalisation of π - bonds

sp^3 hyb:

CH_4, NH_3, H_2O, CH_3Cl, SO_4^{2-}, ClO_4^-



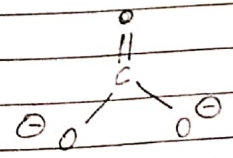
sp^3d hyb: PCl_5

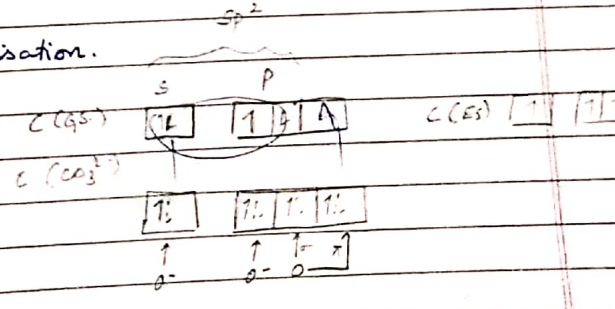


Unsymmetrical structure

sp^3d^2 hyb: SF_6, ICl_4^-

CO_3^{2-}: sp^2 hybridisation.





sp^3d^3 - IF_7

Pentagonal bipyramidal.

Ang. separation ∝ 1/Repulsion

* VSEPR theory:

- Gillespie & Nyholm 1957

Mutual interaction among the e⁻s orients the orbitals in space to an equilibrium position where repulsions are minimum.

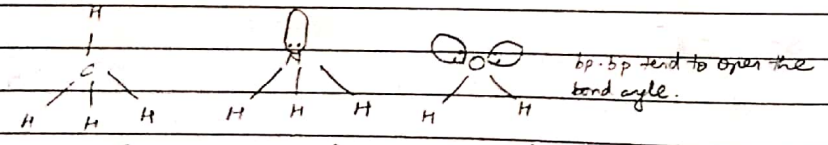
The stereochemistry of the central atom in a molecule is then determined by the repulsive interactions among the e⁻ pairs. (bond pairs & lone pairs)

- LP e⁻s repel each other more strongly than BP e⁻s

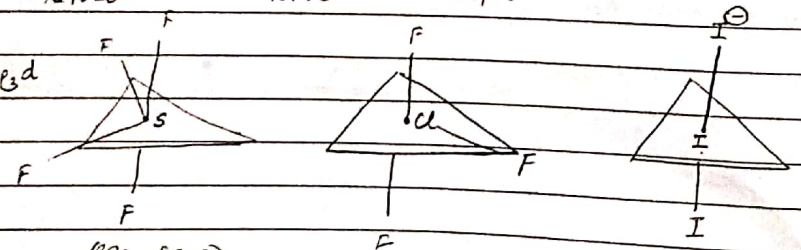
LP - LP > LP - BP > BP - BP

conc. only on the central atom

A L.P is conc. around the central atom, while a B.P is pulled out bet two bonded atoms. As such the repulsion becomes greater when a L.P is involved.

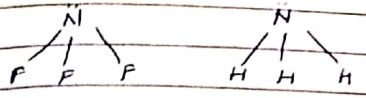


109.28° 107.3° 104.5°



(See-saw) (T-shape) (Linear)

Repulsion by a BP ↓ as EN of the atom bonded to the central atom ↑.



(102°) (107.3°)

- As the bonded atom becomes more EN, the charge is displaced further away from the central atom and repulsion decreases.

- Multiple bond orbitals repel other orbitals more strongly than single bond orbitals.

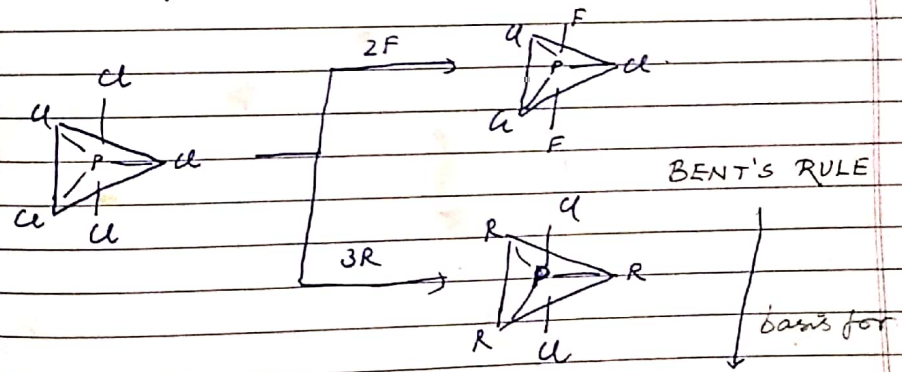
O = PF_3 101.5°

O = PCl_3 103.5°

O = PBr_3 101.5°

- The bond pairs are removed farthest from P atom (moving from Br → F)

bp - bp repulsion becomes minimum & the repulsion from multiple double bond makes the bond angle least.



More EN atoms pulls the shared e⁻ pair towards it & electropositive atoms repel the shared e⁻ pair away from it.

Bent's rule states that more E.N atom or substituent prefer to combine with those hyb. orbitals with less s character & vice versa.

$sp^3d \Rightarrow sp^2 + p_z d_{z^2}$

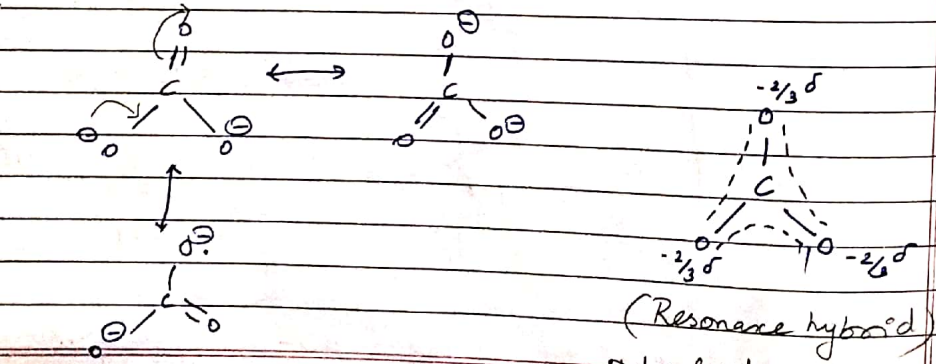
33% s 0% s

Octet rule / Electronic theory of valency: [Kössel & Lewis]
Every element has a tendency to attain inert elec. configuration of the nearest inert gas.

Does not explain,
i) directional nature of covalent bond
ii) bond angles
iii) geometry of certain molecules.

Valence Bond Theory: [Pauling & Slater]

1) A covalent bond are of two types (σ, π) both being formed by orbital overlap.
2) Distortion due to LP (VSEPR)
3) Hybridisation
4) Resonance.



(Resonance hybrid)
Delocalised bonds

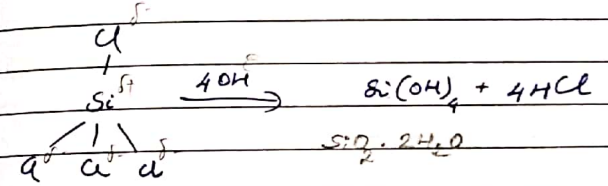
Limitations:
- PCl_5 is not formed acc. to electronic theory of valency.
- PCl_5 is unstable, SF_6 is stable ?
unsymmetrical symmetrical

Peroxide is highly explosive.

$2H_2O_2 \xrightarrow[\text{light}]{\text{decom.}} 2H_2O + O_2\uparrow$

(DISPROPORTIONATION RXN)

- CCl_4 does not hydrolyse CCl_4 → no empty d
$SiCl_4$ does hydrolyse Si - empty d orbitals



$SiCl_4 + 4OH \rightarrow Si(OH)_4 + 4HCl$

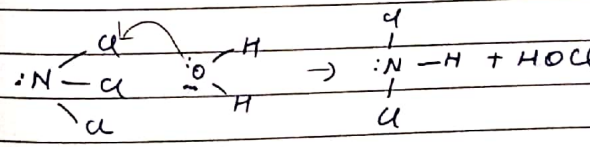
$SiO_2 \cdot 2H_2O$

E.N, C → 2.55
N → 3.04
Cl → 3.16
P → 2.19.

NCl_3, PCl_3 > hydrolyse to give different product

NCl_3 → no empty 3d, attacking on central N is not possible

$N^{3.04}$ $Cl^{3.16}$ E.N diff is small)
(No dev of partial -ve charge)



$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$

$PCl_3 + H_2O \rightarrow P(OH)_3 + 3HCl$

(H_3PO_3)

→ BF_3, CCl_4, CO_2 are all not polar

→ Dipole moments can be explained by VSEPR structures

→ NH_3 is a stronger base than PH_3

* PH_3 does not form complete sp^3 hybridisation
* Down the grp. the diff. in energy b/w 's' & 'p' increases.

Hybridisation takes place when there is a similarity in energy levels b/w bonding orbitals.

3s, 3p, E diff. is higher to prevent effective hybridisation.

P uses pure p orbitals for formation of P-H bonds.

To donate a L.P, it should be directional with the acceptor.