

Hybridization.

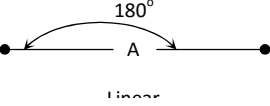
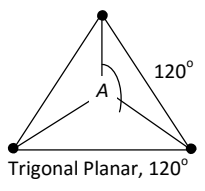
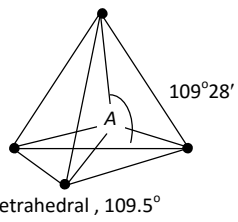
The concept of hybridization was introduced by Pauling and Slater. It is defined as the intermixing of dissimilar orbitals of the same atom but having slightly different energies to form same number of new orbitals of equal energies and identical shapes. The new orbitals so formed are known as hybrid orbitals.

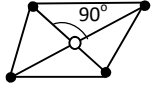
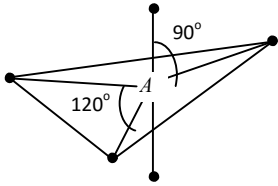
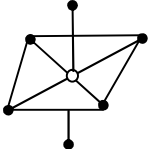
Characteristics of hybridization

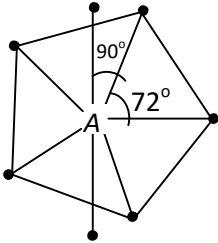
- (1) Only orbitals of almost similar energies and belonging to the same atom or ion undergoes hybridization.
- (2) Hybridization takes place only in orbitals, electrons are not involved in it.
- (3) The number of hybrid orbitals produced is equal to the number of pure orbitals, mixed during hybridization.
- (4) In the excited state, the number of unpaired electrons must correspond to the oxidation state of the central atom in the molecule.
- (5) Both half filled orbitals or fully filled orbitals of equivalent energy can involve in hybridization.
- (6) Hybrid orbitals form only sigma bonds.
- (7) Orbitals involved in π bond formation do not participate in hybridization.
- (8) Hybridization never takes place in an isolated atom but it occurs only at the time of bond formation.
- (9) The hybrid orbitals are distributed in space as apart as possible resulting in a definite geometry of molecule.
- (10) Hybridized orbitals provide efficient overlapping than overlapping by pure s, p and d-orbitals.
- (11) Hybridized orbitals possess lower energy.

Depending upon the type and number of orbitals involved in intermixing, the hybridization can be of various types namely sp, sp², sp³, sp³d, dsp², sp³d², sp³d³. The nature and number of orbitals involved in the above mentioned types of hybridization and their acquired shapes are discussed in following table

Type of hy-	Character	Geometry of molecules as per	No. of	No. of lone	Actual shape of	Example
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hybridisation		VSEPR theory	bonded atoms	lone pairs	molecular shape	
sp	s-character=50%, p-character= 50%		2	0	Linear	$CO_2, HgCl_2, BeF_2, ZnCl_2, MgCl_2, C_2H_2, HCN, BeH_2, C_2H_2, CS_2, N_2O, Hg_2Cl_2, [Ag\{NH_3\}_2]^+$
sp^2	s-character= 33.33%, p-character=66.67%		3	0	Trigonal Planar	$BF_3, AlCl_3, SO_3^{2-}, C_2H_4, NO_3^-, CO_3^{2-}, HCHO, C_6H_6, CH_3^+$ graphite, $C_2Cl_4, C_2H_2Cl_2, [HgI_3]^-, [Cu(PMe_3)_3]^+$
		<120°	2	1	V-shape (bent)	$NO_2^-, SO_2, SnCl_2$
sp^3	s-character = 25%, p-character = 75%		4	0	Tetrahedral	$CH_4, SiH_4, SO_4^{2-}, SnCl_4, ClO_4^-, BF_4^-, NH_4^+, CCl_4, SiF_4, H_2 - NH_2, [BeF_4]^{2-}, XeO_4, [AlCl_4]^-, [SnCl_4], PH_4^+, Diamond, silica, Ni(CO)_4, Si(CH_3)_4, SiC, SF_2, [NiCl_4]^{2-}, [MnO_4]^{2-}, [VO_4]^{3-}$
		< 109.5°	3	1	Trigonal pyramidal	$NH_3, PCl_3, PH_3, AsH_3, ClO_3^-, POCl_3, H_3O^+, XeO_3$
		104.5°	2	2	V-shape (bent)	$H_2O, H_2S, PbCl_2, OF_2, NH_2^-, ClO_2$

dsp^2	s-character = 25% p – character = 50% d – character = 25%	 Square planar	4	0	Square planar	$[Cu(NH_3)_4]^{2+}$, $[Ni(CN)_4]^{2+}$ $[Pt(NH_3)_4]^{2+}$
sp^3d	s-character = 20%, p-character = 60%, d-character = 20%	 Trigonal bipyramidal	5	0	Trigonal bipyramidal	PCl_5 , $SbCl_5$, XeO_3F_2 , PF_5 AsF_5 , PCl_4^+ , PCl_6^- , $[Cu(Cl)_5]^{3-}$ $[Ni(CN)_5]^{3-}$, $[Fe(CO)_5]$
			4	1	Irregular tetrahedral	$TeCl_4$, SF_4
			3	2	T-shaped	ClF_3 , IF_3
			2	3	Linear	I_3^- , XeF_2
sp^3d^2	s-character = 25% p – character = 50% d – character = 25%	 Octohedral	6	0	Octahedral	SF_6 , PF_6^- , $SnCl_6^-$, MoF_6 , $(BaCl_6)^-$, $(PF_6)^-$, $[Fe(CN)_6]^{4-}$, $[Fe(H_2O)_6]^{3+}$
			5	1	Square pyramidal	ICl_5 , BrF_5 , IF_5 , $XeOF_4$

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			4	2	Square planar	$\text{XeF}_4, \text{ICl}_4^-$
sp^3d^3	s-character = 14.28%, p-character = 42.86%, d-character = 42.86%	 Pentagonal bipyramidal	7	0	Pentagonal bipyramidal	$\text{IF}_7, [\text{ZrF}_7]^{3-}, [\text{UF}_7]^{3-}$ $[\text{UO}_2\text{F}_5]^{3-}$
			6	1	Distorted octahedral	XeF_6

Short trick to find out hybridization : The structure of any molecule can be predicted on the basis of hybridization which in turn can be known by the following general formulation.

$$H = \frac{1}{2}(V + M - C + A)$$

Where H = Number of orbitals involved in hybridization viz. 2, 3, 4, 5, 6 and 7, hence nature of hybridization will be sp, sp², sp³, sp³d, sp³d², sp³d³ respectively.

V = Number electrons in valence shell of the central atom,

M = Number of monovalent atom

C = Charge on cation,

A = Charge on anion

Few examples are given below to illustrate this:

Type : (A) When the central atom is surrounded by monovalent atoms only, e.g. BeF₂, BCl₃, CCl₄, NCl₃, PCl₅, NH₃, H₂O, OF₂, TeCl₄, SCI₂, IF₇, ClF₃, SF₄, SF₆, XeF₂, XeF₄, etc. Let us take the case of PCl₅. $H = \frac{1}{2}(5 + 5 - 0 + 0) = 5$. Thus, the type of hybridization is sp³d.

Type : (B) When the central atom is surrounded by divalent atoms only; e.g. CO₂, CS₂, SO₂, SO₃, XeO₃ etc. Let us take the case of SO₃. $H = \frac{1}{2}(6 + 0 - 0 + 0) = 3$. Thus, the type of hybridization in SO₃ is sp².

Type : (C) When the central atom is surrounded by monovalent as well as divalent atoms, e.g. COCl₂, POCl₃, XeO₂F₂ etc. Let us take the case of POCl₃. $H = \frac{1}{2}(5 + 3 - 0 + 0) = 4$. Thus, the nature of hybridization in POCl₃ is sp³.

Type : (D) When the species is a cation, e.g. NH₄⁺, CH₃⁺, H₃O⁺ etc. Let us take the case of CH₃⁺. $H = \frac{1}{2}(4 + 3 - 1 + 0) = 3$. Thus, the hybridization in CH₃⁺ is sp².

Type : (E) When the species is an anion, e.g. SO₄²⁻, CO₃²⁻, PO₄³⁻, NO₂⁻, NO₃⁻, etc. Let us take the case of SO₄²⁻. $H = \frac{1}{2}(6 + 0 - 0 + 2) = 4$. Thus, hybridization in SO_4^{2-} is sp³.

Type : (F) When the species is a complex ion of the type ICl₄⁻, I₃⁻, ClF₂⁻, etc. Let us take the case of ClF₂⁻. $H = \frac{1}{2}(7 + 2 - 0 + 1) = 5$. Thus, in ClF₂⁻, Cl is sp³d hybridized.

Type : (G) When the species is a complex ion of the type [PtF₆]²⁻, [Co(NH₃)₆]²⁺, [Ni(NH₃)₄Cl₂] etc. In such cases nature of hybridization is given by counting the co-ordination number.

Important Tips

The sequence of relative energy and size of s – p type hybrid orbitals is sp < sp² < sp³.

The relative value of the overlapping power of sp, sp² and sp³ hybrid orbitals are 1.93, 1.99 and 2.00 respectively.

An increase in s-character of hybrid orbitals, increases the bond angle. Increasing order of s-characters and bond angle is sp³ < sp² < sp.

Normally hybrid orbitals (sp, sp², sp³, dsp², dsp³ etc.) form σ-bonds but in benzyne lateral overlap of sp²-orbitals forms a π-bond.

Some iso-structural pairs are [NF₃, H₃O⁺], [NO₃⁻, BF₃], [SO₄²⁻, BF₄⁻]. There structures are similar due to same

hybridization.

In BF₃ all atoms are co-planar.

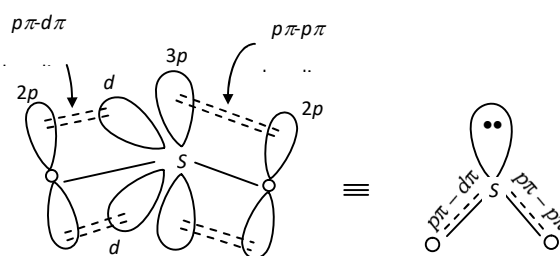
In PCl₅ the state of hybridization of P atom is sp³d. In its trigonal bipyramidal shape all the P-Cl bonds are not equal.

The π bond formed between S and O atoms in SO₂ molecule is due to overlap between their p-orbitals ($P\pi - P\pi$ bonding) or between p orbital of O-atom with d-orbital of S-atom (called $p\pi - d\pi$ bonding)

$$_{16}\text{S} = 1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1 \quad (\text{Ground state configuration})$$

$$= 1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1 3d^1 \quad (\text{Excited state configuration})$$

$$_8\text{O} = 1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$$



S-atom undergoes sp² hybridization leaving one half-filled 3p_z orbital and one d-orbital unhybridized. Out of two half filled orbitals of O-atom, one is involved in formation of σ -bond with S-atom and the other in forming π -bond.
