

NEET/JEE 2019

Focus more to get high rank in NEET/JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

Unit-2 : Classification of Elements and Periodicity in Properties | Chemical Bonding and Molecular Structure

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

HISTORY OF THE PERIODIC TABLE

Earlier Attempts

Dobereiner's Triads

In the triad of elements, the atomic weight of middle element is the arithmetic mean of other two.

Newland's Law of Octaves

Elements are arranged in increasing order of their atomic weights, the properties of every eighth element are similar to the first one.

Mendeleev's Periodic Table

Elements are arranged such that the properties of the elements are the periodic function of their atomic weights. Table contains 8 groups and 7 periods.

MODERN PERIODIC TABLE

Modern Periodic Law

- The physical and chemical properties of elements are periodic function of their atomic numbers.
- Elements are arranged in order of increasing atomic numbers.
- It has seven horizontal rows known as periods and eighteen vertical columns known as groups.

Elements in Periodic Table

s-block elements

- Group-1 to 2
- E.C. : ns^{1-2}
- Group-1 elements form M^+ ions.
- Group-2 elements form M^{2+} ions.

p-block elements

- Group -13 to 18
- E.C. : $ns^2 np^{1-6}$ (excluding helium)
- Except noble gases and fluorine, all other elements show variable oxidation states.

d-block elements

- Group - 3 to 12
- Lies between s- and p-block elements
- E.C. : $(n-1)d^{1-10} ns^{0-2}$
- Show variable valencies and oxidation states.

f-block elements

- 4f-series : lanthanides
- 5f-series : actinides
- E.C. : $(n-2)f^{1-14} (n-1)d^{0-1} ns^2$
- Variable oxidation states, most common in +3.

PERIODIC TRENDS

Atomic Radius

- **Crystal or metallic radius** : It is one-half of the internuclear distance between the two nearest atoms in the metallic lattice. It is generally used for metals.
- **van der Waals' radius** : It is one-half of the internuclear distance between the two adjacent identical atoms belonging to two neighbouring molecules of an element.
- **Covalent radius** : It is one-half of the distance between the centres of the nuclei of two similar atoms joined by a single covalent bond. This is generally used for non-metals.
 - The atomic radii of noble gases or inert gases are, in fact, van der Waals' radii since they do not form molecules.
 - van der Waals' radius > metallic radius > covalent radius (for an atom)

Ionic Radius

- It is the distance between the nucleus and the point where the nucleus exerts its influence on the electron cloud.
 - Cation is smaller and anion is larger than the parent atom of the element. In case of isoelectronic ions, the size decreases with increase in the nuclear charge.

Ionisation Enthalpy

- It is the energy required to remove an electron from an isolated gaseous atom in its ground state.

$$M_{(g)} + I.E. \rightarrow M_{(g)}^{+} + e^{-}$$
- $I.E. \propto \frac{1}{\text{size of atom}} \propto \text{Effective nuclear charge}$

$$\propto \frac{1}{\text{Screening effect}}$$
- Completely or half-filled orbital has higher I.E. because of higher stability.

Electron Gain Enthalpy

- It is the amount of energy released when an electron is added to an isolated gaseous atom.

$$A_{(g)} + e^{-} \rightarrow A_{(g)}^{-}; \Delta_{eg} H$$
- $\Delta_{eg} H \propto \frac{1}{\text{Size of atom}} \propto \text{Effective nuclear charge}$

$$\propto \frac{1}{\text{Screening effect}}$$

Electronegativity

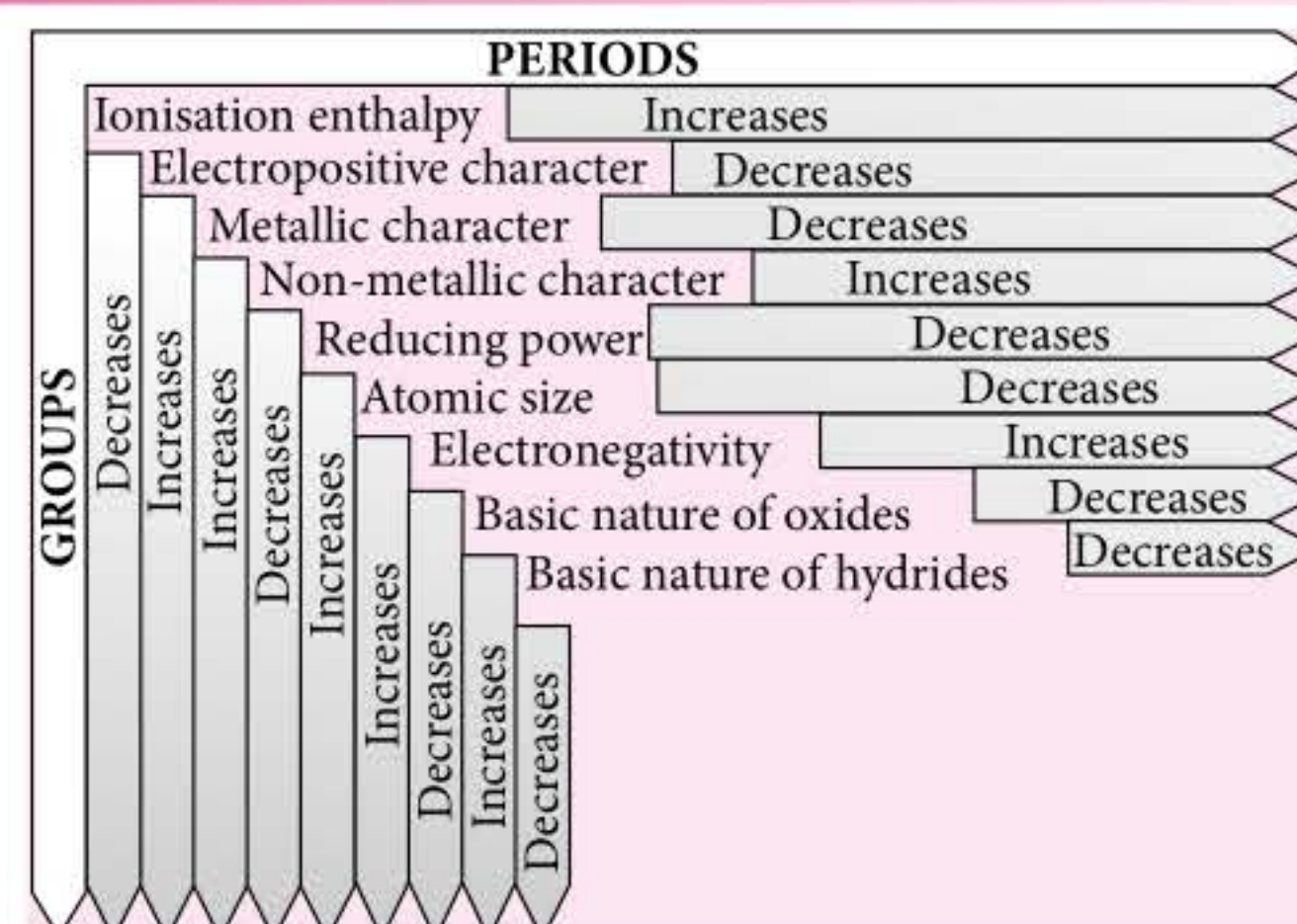
- It is the tendency of an atom to attract the shared pair of electrons towards itself in a covalent bond.
- Mulliken scale of electronegativity

$$\chi = \frac{1}{2} [\Delta_i H + \Delta_{eg} H]$$
- Pauling scale of electronegativity

$$\chi_A - \chi_B = 0.1017 \sqrt{\Delta}$$
 where, $\Delta = E_{A-B} - \frac{1}{2} \sqrt{E_{A-A} + E_{B-B}}$
 Here, E represents bond dissociation enthalpy (in kJ mol^{-1}).
- Percentage of ionic character

$$= 16(\chi_A - \chi_B)^2 + 3.5(\chi_A - \chi_B)^4$$
 - If $\chi_A - \chi_B = 1.7$, bond is 50% covalent and 50% ionic.
 - If $\chi_A - \chi_B > 1.7$, bond is predominately ionic.
 - If $\chi_A \approx \chi_B$, A — B bond is purely covalent.

SUMMARY OF SOME GENERAL TRENDS



CHEMICAL BONDING AND MOLECULAR STRUCTURE

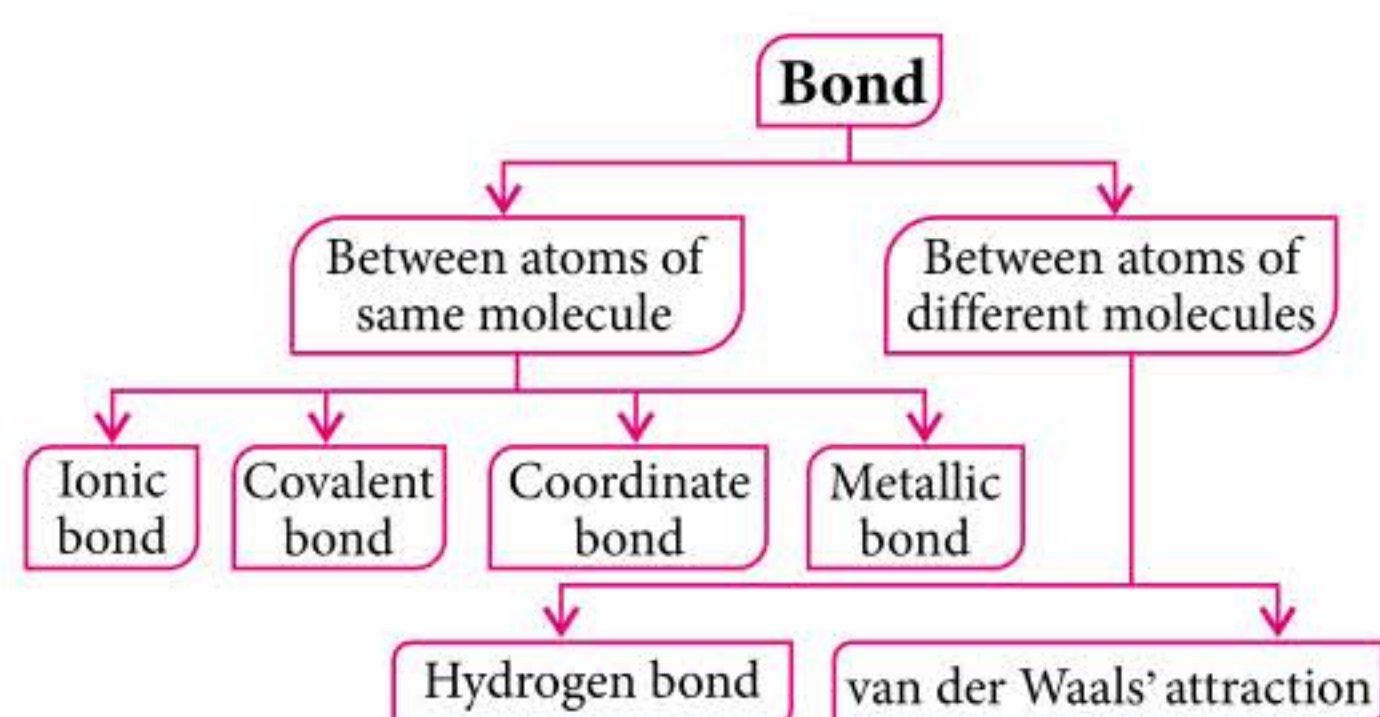
The phenomenon of union of two or more atoms involving redistribution of electrons, so that each atom involved in bonding acquires stable configuration in order to gain stability is known as chemical bonding.

- Atoms form bonds since it leads to decrease in energy.
- Whenever atoms come close, both attractive and repulsive forces operate and if the magnitude of attractive forces is more than those of repulsive forces, a chemical bond is formed.

KÖSSEL-LEWIS APPROACH TO CHEMICAL BONDING

Atoms can combine either by transfer of valence electrons from one atom to another or by sharing of valence electrons in order to have an octet in their valence shell (octet rule).

TYPES OF BOND



Bond Formation

- Nature of bond formed between two atoms depends upon electropositive and electronegative character of bonded atoms.
 - **Ionic bond** : Electropositive element + Electronegative element
 - **Covalent bond** : Electronegative element + Electronegative element
 - **Metallic bond** : Electropositive element + Electropositive element
- Ionic bond is non-directional in nature while covalent bonds are directional in nature.

IONIC BOND

- The bonds formed between atoms by transferring of valence electrons from one atom to another

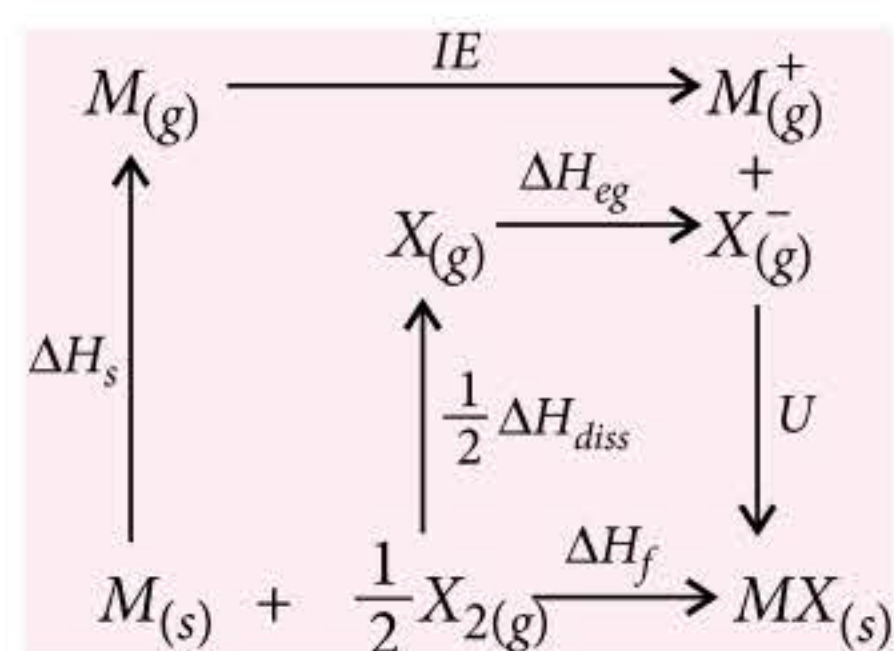
is said to be electrovalent or ionic bond, and the compound so formed is an ionic compound.

- **Conditions for the formation of electrovalent bond :**

- **Number of valence electrons** : The atom which changes to a cation must contain 1, 2 or 3 valence electrons and the one changing to anion must contain 5, 6 or 7 valence electrons.
- **Electronegativity difference** : Higher the electronegativity difference between the atoms, more ionic will be the bond formed.
- **Low ionisation energy** : Ionisation energy of the element forming the cation *i.e.*, metal, should be low.
- **High electron affinity** : Electron affinity of the element forming anion *i.e.*, non-metal, should be high.
- **High lattice energy** : Higher the lattice energy, greater is the ease of formation of ionic compound.

BORN HABER CYCLE

- Born Haber cycle is based on Hess's law of constant heat summation and it correlates the energy changes taking place in various steps involved in the formation of ionic compounds.
- The steps can be represented in the cycle as :



$$\Delta H_f = \Delta H_s + IE + \frac{1}{2} \Delta H_{diss} + \Delta H_{eg} + U$$

where, ΔH_f = Enthalpy of formation,
 ΔH_s = Enthalpy of sublimation,
 IE = Ionisation energy,
 ΔH_{diss} = Enthalpy of dissociation,
 ΔH_{eg} = Electron gain enthalpy
 and U = Lattice energy.

COVALENT BOND

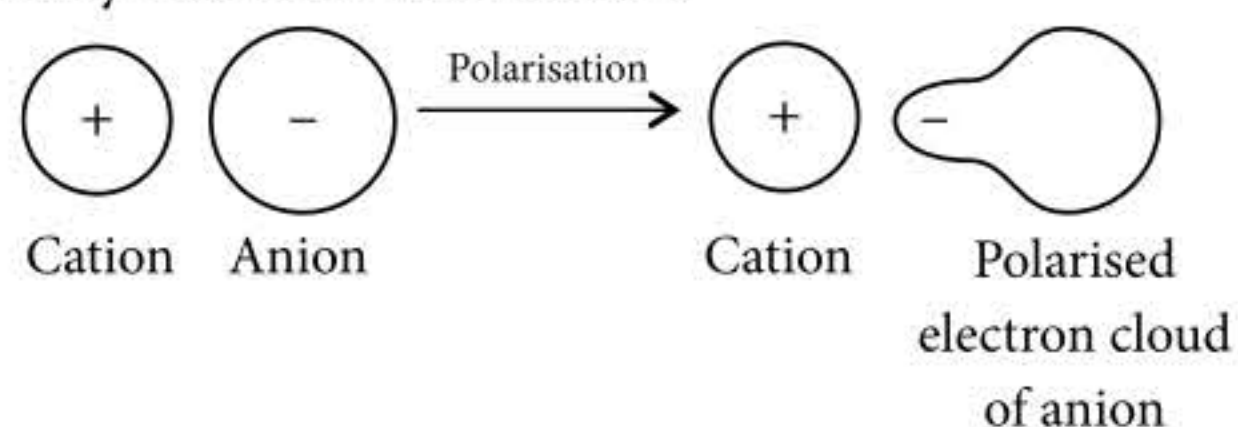
- Bond formed by sharing of electrons between the combining atoms is called covalent bond and the compound so formed is a covalent compound.

COORDINATE BOND

- A covalent bond in which both electrons of the shared pair are contributed by one of the atoms only, is called a coordinate bond or dative bond and the compound is called a coordinate compound.

POLARISATION

- **Fajan's rule** : In ionic bond, some covalent character is introduced because of the tendency of the cation to polarise the anion. In fact, cation attracts the electron cloud of the anion and pulls electron density between two nuclei.



- **According to Fajan's rule :**
 - Smaller the size of cation, larger is its polarising power.
 - Larger the size of anion, more will be its polarisability.
 - More the charge on cation and anion, more is the covalent character.
 - Cations having 18 electrons in outermost shell bring greater polarisation than the other which have 8 electrons in outermost shell.

IMPORTANT TERMS AND FORMULAE

- Formal charge of an atom in a Lewis structure = Total no. of electrons in the free atom - Total no. of electrons of lone pairs (non-bonding electrons) - $\frac{1}{2} \times$ Total no. of shared electrons (bonding electrons)

$$\text{i.e., } F = V - L - \frac{1}{2} S$$

- **Bond length** : Equilibrium distance between the nuclei of two bonded atoms in a molecule.
 - Bond length \propto size of atoms, $\propto \frac{1}{\text{bond order}}$
- **Bond angle** : Angle between the orbitals containing

bonding electron pairs around the central atom in a molecule/complex ion.

- **Bond enthalpy** : Amount of energy required to break one mole of bonds between two atoms in a gaseous state.
- **Bond order** : Number of bonds formed between two atoms in a covalent compound.
- **Resonance** : The phenomenon of existence of a molecule in different structural forms, each of which can explain most of the properties of the molecule but none can explain all the properties of the molecule.
- Dipole moment (μ) = Charge \times Distance of separation

THEORIES OF COVALENT BONDING

VSEPR Theory (Nyholm and Gillespie)

- The shape of a molecule depends upon the number of valence shell electron pairs (bonded or non bonded) surrounding the central atom.
- Electron pairs tend to occupy such positions in space which minimise repulsions.
- The repulsive interactions of electron pairs decrease in the order : $lp - lp > lp - bp > bp - bp$

Valence Bond Theory (Pauling)

- A bond is formed between two atoms when the forces of attraction are greater than forces of repulsion.
- A covalent bond is formed between two atoms by pairing of electrons present in the valence shell having opposite spins.
- During bond formation, only valence electrons lose their identity.
- Bond formation is accompanied by release of energy and this accounts for the stability of bond.
- Sigma (σ) bond is formed by the head on overlap of atomic orbitals.
- Pi (π) bond is formed by lateral overlap of half-filled atomic orbitals, perpendicular to internuclear axis.

Molecular Orbital Theory (F. Hund and R.S. Mulliken)

- Molecular orbitals are formed by the linear combination of atomic orbitals.
- The number of molecular orbitals formed is equal to the number of atomic orbitals combined.

- When two atomic orbitals combine they form one bonding molecular orbital of lower energy and one anti-bonding molecular orbital of higher energy.
- The molecular orbitals are filled in accordance with Aufbau principle, Pauli's exclusion principle and Hund's rule.
- Energy order for molecular orbitals upto N_2 is

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x$$

$$= \pi 2p_y < \sigma 2p_z < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$$
- Energy order for molecules beyond N_2

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x$$

$$= \pi 2p_y < \pi^* 2p_x = \pi^* 2p_y < \sigma 2p_z$$
- Bond order (B.O.) = $\frac{1}{2} (N_b - N_a)$
 where, N_b is number of electrons present in BMO and N_a is number of electrons present in ABMO
 - If $N_b > N_a$; B.O. = +ve, the molecule is stable.
 - If $N_b < N_a$; B.O. = -ve, the molecule is unstable or does not exist.

- If $N_b = N_a$; B.O. = 0, the molecule is unstable or does not exist.
- Isoelectronic species have same bond order.

HYBRIDISATION

- Hybridisation is a hypothetical phenomenon. It is introduced to explain shapes of molecules and bonding parameters such as bond angle, strength of bonds.
- The structure of a molecule can be predicted on the basis of hybridisation by using the formula :

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

where, H = number of orbitals involved in hybridisation, V = number of electrons in valence shell of the central atom, M = number of monovalent atom, C = charge on cation and A = charge on anion.

IIT-Delhi tops MHRD mandate, enrolls 16% girls in all its courses

At a time when engineering institutes are struggling to admit girls, IIT-Delhi has touched an all-time high number of female students this year. The HRD ministry had mandated that all 23 IITs increase the enrolment of girls to 14% in 2018. IIT-Delhi has already recorded a 16% enrolment of girls in every course, before the admission season gets over.

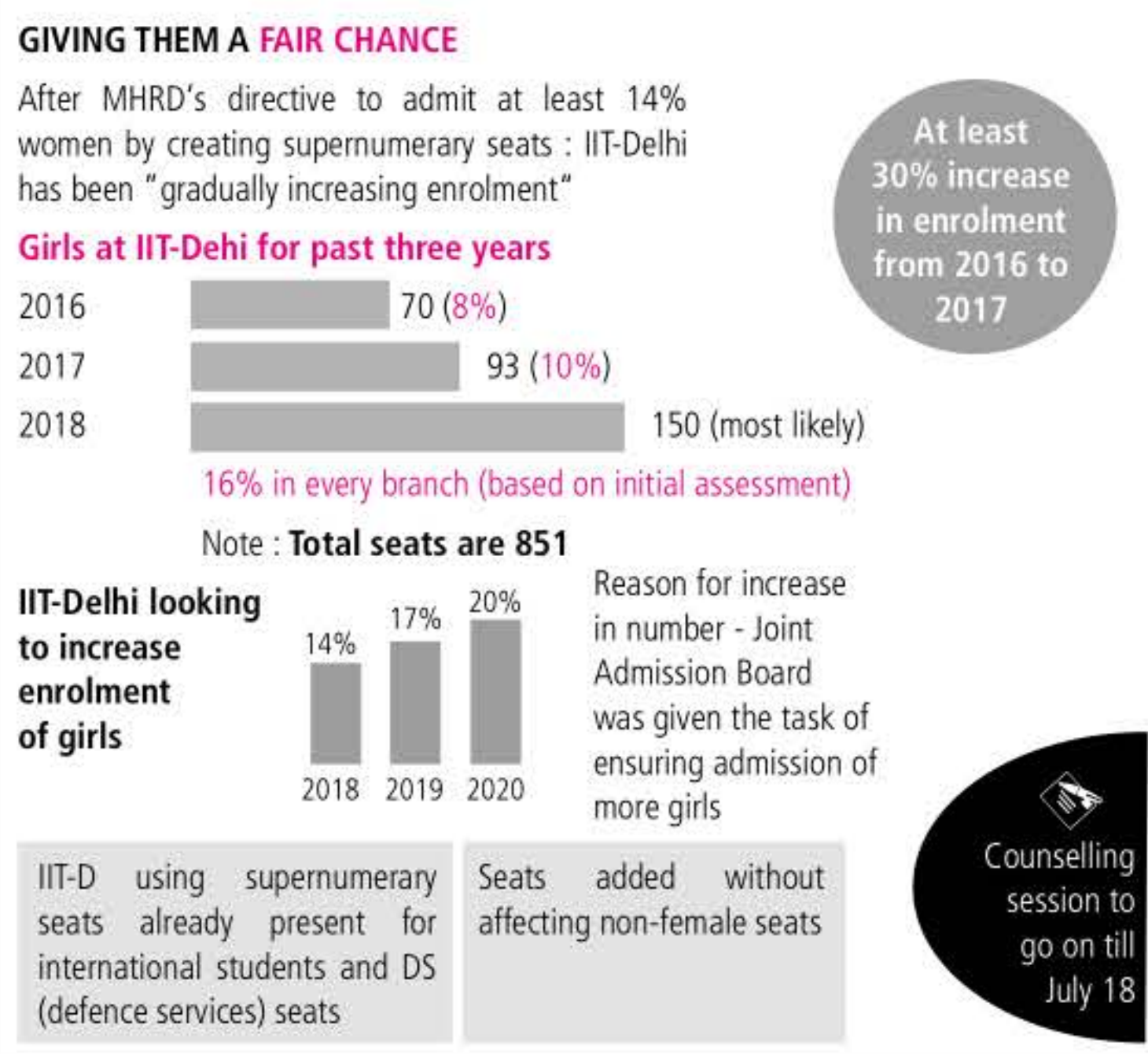
"Our faculty members conducted special interaction sessions with all JEE-qualified girl students and their parents both last year and this year to explain the prospects of studying at IIT," said Aditya Mittal, professor and chairman of Joint Entrance Examination-Advanced at IIT-Delhi.

The sessions for two consecutive years are already showing results. In 2016, IIT-D admitted 70 girls, which increased by over 30% to 93 in 2017 and this year it is likely to reach 150 out of a total 851 seats.

The idea behind the initiative was to help qualified female candidates make their choices during the JEE/JoSAA (Joint Seat Allocation Authority) 2018 counselling process. "The session saw over 150 students attending it where not just faculty members, but even student mentors interacted with potential candidates," Mittal said.

Asked why fewer girls enrol in IITs despite getting good ranks, Mittal attributed it to several factors. "Our IIT-Mandi director Timothy Gonsalves in his four-year research found that there are many girls who get good ranks in JEE Advance but don't enrol in IITs. Several parents we interacted with had the perception that engineering sectors like mechanical and chemical are not viable for girl students. Many avoid IITs as they prefer institutes closer to their homes," he added.

There were some parents who didn't agree to send their daughters for specialised preparations as they would do for boys. "The central idea to bring in more girls was based on the IIT ethos that we don't provide literacy but education. It is also because we revise curriculum frequently. While 40% of our curriculum is core, 60% are electives chosen by the students," Mittal said.



"We at IIT-Delhi are vying for more than 14% girl students this year. We want to enrol 17% in 2019 and 20% in 2020. Eventually, we hope that these steps would be enough to encourage more girl students to join the institute," said Mittal.

The chairman of the JEE counselling said that the increase in enrolment will not be radical but gradual. "We have limited space in hostels, laboratories and classrooms and this endeavour will not be affecting the seats already allotted for non-female students," Mittal added.



Courtesy : The Times of India

MOLECULES HAVING BOND PAIRS ONLY

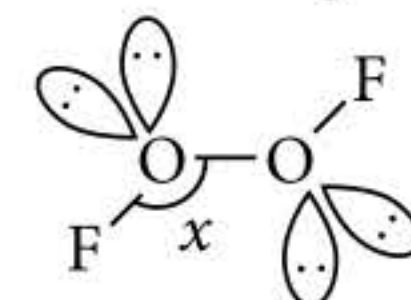
Type of hybridisation	No. of hybrid orbitals	Shape of molecule	Bond angle	Examples
sp	2	Linear	180°	BeCl_2 , BeF_2 , CO_2
sp^2	3	Trigonal planar	120°	BF_3 , BCl_3
sp^3	4	Tetrahedral	109.5°	CH_4 , CCl_4
dsp^2	4	Square planar	90°	$[\text{Ni}(\text{CN})_4]^{2-}$ $[\text{PtCl}_4]^{2-}$
dsp^3 or sp^3d	5	Trigonal bipyramidal	120° and 90°	PCl_5 , PF_5
d^2sp^3 or sp^3d^2	6	Octahedral	90°	SF_6
d^3sp^3 or sp^3d^3	7	Pentagonal bipyramidal	72° and 90°	IF_7

MOLECULES HAVING BOND PAIRS AND LONE PAIRS

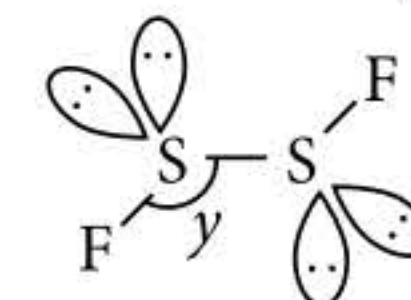
Type of molecule	Hybridisation	Bond angle	Actual shape	Examples
AB_2L	sp^2	$<120^\circ$	V-shape or Bent	SO_2 , PbCl_2
AB_2L_2	sp^3	$<109^\circ28'$	V-shape or Bent	H_2O , Cl_2O
AB_2L_3	sp^3d	180°	Linear	XeF_2
AB_3L_2	sp^3d	90°	T-shape	ClF_3
AB_3L_1	sp^3	$<109^\circ28'$	Trigonal pyramidal	NH_3 , PCl_3
AB_4L_1	sp^3d	$120^\circ, 90^\circ$	See saw or Distorted tetrahedron	SF_4 , SCl_4
AB_4L_2	sp^3d^2	90°	Square planar	XeF_4
AB_5L_1	sp^3d^2	$<90^\circ$	Square pyramidal	IF_5
AB_6L_1	sp^3d^3	–	Distorted octahedral	XeF_6

SPEED PRACTICE

- Which of the following geometry is not possible when the central atom is having sp^3d -hybridization?
 - Trigonal bipyramidal
 - Trigonal planar
 - Linear
 - T-shaped
- Five ionization energy values in kJ/mol are listed below:
 $E_1 = 870$, $E_2 = 830$, $E_3 = 1010$, $E_4 = 1290$, $E_5 = 376$.
 These are
 - successive ionization energies for the element with atomic number 5
 - the first *I.E.* of successive elements in group 15, 16, 17, 18 and 1 respectively
 - the first *I.E.* of elements with atomic number 1 to 5
 - successive *I.E.* for transition elements with four electrons in *d*-subshell.
- Which of the following statements are true (T) or false (F)?
 - In SnCl_2 the bonding takes place in ground state and the bond angle Cl—Sn—Cl is slightly less than 120° .
 - The molecular geometry of XeF_7^+ is pentagonal bipyramidal having two different Xe—F bond lengths.
 - In SF_4 , the bond angles, instead of being 90° and 120° are 89° and 117° respectively due to the presence of a lone pair.
 - T T T
 - F T T
 - T T F
 - T F T
- Generally, the first ionisation energy increases along a period. But there are some exceptions. The one which is not an exception is
 - Na and Mg
 - Be and B
 - N and O
 - Mg and Al.
- The bonds present in $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ are
 - ionic
 - covalent
 - co-ordinate
 - all of these.
- Compare bond angles for the following molecules :



x



y