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# Classification of Elements and Periodicity in Properties **Chemical Bonding and Molecular Structure**

Classification of Elements and Periodicity in Properties

#### GENESIS OF PERIODIC CLASSIFICATION

- Dobereiner's Triads: The element in a triad has similar properties and the atomic weight of the middle element of each triad is very close to the arithmetic mean of atomic weight of the other two elements.
- De Chancourtois Classification: The elements were arranged in order of increasing atomic weights and a cylindrical table of elements was proposed to display the periodic recurrence of properties.
- Newland's Law of Octaves: When the elements are arranged in the increasing order of atomic weights, the properties of every eighth element were similar to the first one like the eighth note of a musical scale.
- Lothar Meyer's Arrangements: When the properties of the elements such as atomic volume, m.pt., b.pt., etc., are plotted as a function of their atomic weights, the elements with similar properties occupied almost similar positions on the curve.

#### Mendeleev's Periodic Table

- The physical and chemical properties of elements are a periodic function of their atomic weights.
- Characteristics of Mendeleev's Periodic Table:
  - (i) Eight vertical columns, called groups.
  - (ii) Six horizontal rows, called periods.

- Significance of Mendeleev's Periodic Table :
  - Instead of studying properties of elements separately, they can be studied in groups containing elements with same properties.
  - At his time only 63 elements were known. He left blank spaces or gap for unknown elements.
  - Mendeleev's periodic table corrected the doubtful atomic weights.

#### MODERN PERIODIC TABLE

- According to Moseley "physical and chemical properties of elements are the periodic functions of their atomic numbers".
- Cause of Periodicity: The cause of periodicity in properties is the repetition of similar outer electronic configurations after certain regular intervals.
- Long form of periodic table consists of seven horizontal rows called 'periods' and eighteen vertical columns called 'groups'.
- There are some common names given to few groups also:
  - Elements of group-1 are called *alkali metals*.
  - Elements of group-2 are called alkaline earth metals.

- Elements of group-11 are called *coinage metals*.
- Elements of group-15 are called *pnictogens*.
- Elements of group-16 are called *chalcogens*.
- Elements of group-17 are called *halogens*.
- Elements of group-18 are called noble gases or inert gases.
- **IUPAC Nomenclature of Elements with Atomic** Number 100: The name of an element is derived directly from its atomic number using the numerical root for 0 to 9. These roots are tabulated below.

#### Notation for IUPAC nomenclature of elements

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	О
9	enn	e

#### ELECTRONIC CONFIGURATIONS AND TYPES **ELEMENTS**

- s-Block Elements: Elements in which the last electron enters the s-orbital of their respective outermost shells are called *s-block elements*. General outer shell electronic configuration of s-block elements is  $ns^{1-2}$ , where, n = 2-7.
- **p-Block Elements**: Elements in which the last electron enters any one of the three p-orbitals of their respective outermost shells are called p-block elements. General outer shell electronic configuration of p-block elements is  $ns^2np^{1-6}$ , where n = 2-7.
- d-Block Elements: Elements in which the last electron enters any one of the five d-orbitals their respective penultimate shells are called *d-block* elements. General outer shell electronic configuration of d-block elements is  $(n-1)d^{1-10}ns^{0-2}$ , where n = 4-7.
- f-Block Elements: Elements in which the last electron enters any one of the seven f-orbitals of their respective anti-penultimate shells are called

f-block elements. General outer shell electronic configuration of f-block elements is  $(n-2)f^{1-14}$  $(n-1)d^{0-1} ns^2$ , where n = 6-7.

# PEEP INTO PREVIOUS YEARS

- The element with Z = 120 (not yet discovered) will be an/a
  - (a) inner-transition metal
  - alkaline earth metal
  - alkali metal
  - (d) transition metal.

(JEE Main 2019)

- The element Z = 114 has been discovered recently. It will belong to which of the following family/group and electronic configuration?
  - (a) Carbon family, [Rn]  $5f^{14} 6d^{10} 7s^2 7p^2$
  - (b) Oxygen family, [Rn]  $5f^{14} 6d^{10} 7s^2 7p^4$

  - (c) Nitrogen family, [Rn]  $5f^{14} 6d^{10} 7s^2 7p^6$ (d) Halogen family, [Rn]  $5f^{14} 6d^{10} 7s^2 7p^5$

(NEET 2017)

- An element *X* belongs to fourth period and fifteenth group of the periodic table. Which of the following statements is true?
  - (a) It has a completely filled s-orbital and a partially filled *d*-orbital.
  - (b) It has completely filled s-and p-orbitals and a partially filled *d*-orbital.
  - (c) It has completely filled s-and p-orbitals and a half-filled *d*-orbital.
  - (d) It has a half-filled p-orbital and completely filled *s*-and *d*-orbitals. (WB JEE 2016)

#### Periodic Trends in Properties of Elements

- Atomic Radii: Distance from the centre of the nucleus to the outermost shell of electrons. Types of atomic radii:
  - Covalent radius: One half of the distance between the centre of nuclei of two similar atoms bonded by a single covalent bond.
  - Metallic radius: One half of the internuclear distance between the two neighbouring atoms of a metal in the metallic lattice.
  - van der Waals' radius : van der Waals' radius is one half of the distance between nuclei of two identical non-bonded isolated atoms. Noble gases held by weak van der Waals' forces of attraction.
- Variation of Atomic Radii in the Periodic Table
  - **Variation in a period :** The atomic radii ↓ with in atomic number on going from left to right due to the increase of effective nuclear charge.

- Variation in a group: The atomic radii of elements \(^1\) from top to bottom in a group. On moving down a group, the effective nuclear charge  $\downarrow$  with  $\uparrow$  in atomic number.
- Ionic Radii: The effective distance from the centre of the nucleus of the ion up to which it exerts its influence on its electronic cloud.
  - The ionic radii share the same trends as atomic radius.
  - The radius of positive ion (cation) is always smaller than that of the parent atom because it has lesser electrons but same nuclear charge.
  - The radius of negative ion (anion) is larger than that of the parent atom because extra electrons are added due to which repulsion among electrons increases and effective nuclear charge decrease.
- Isoelectronic Species: Atoms or ions having the same number of electrons but different magnitude of nuclear charge. e.g., O<sup>2-</sup>, F<sup>-</sup>, Na<sup>+</sup> and Mg<sup>2+</sup> have 10 electrons.
- **Ionisation Enthalpy**: It is the energy required to remove an electron from an isolated gaseous atom in its ground state.

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

If gaseous atom is to lose more than one electrons, they can be removed only one after another i.e., in succession and not simultaneously. This is known as successive ionisation energy or potential:

$$I.E_3 > I.E_2 > I.E_1$$

- The screening effect or shielding effect : In a multielectron atom, valence shell electrons experience less attractive force from the nucleus due to repulsion between inner shell electrons and valence electrons. This is called screening effect or shielding effect.
- Factors affecting ionisation enthalpy:
  - Size of atom :  $I.E. \propto \frac{1}{\text{Size of atom}}$
  - **Nuclear charge :**  $I.E. \infty$  Nuclear charge
  - Screening effect :  $I.E. \propto \frac{1}{\text{Screening effect}}$
  - Completely filled or half-filled orbitals : It is comparatively difficult to remove the electrons from these orbitals (being more stable).

- Type of electrons involved: Ionisation energy decreases in the order of s > p > d > f-orbitals.
- Ionisation energy decreases down the group due to increase in size of the atom and screening effect of intervening electrons.
- Electron Gain Enthalpy: It may be defined as the amount of energy released when an electron is added to an isolated gaseous atom of the element.

$$A_{(g)} + e^{-} \longrightarrow A_{(g)}^{-}; \Delta_{eg}H$$

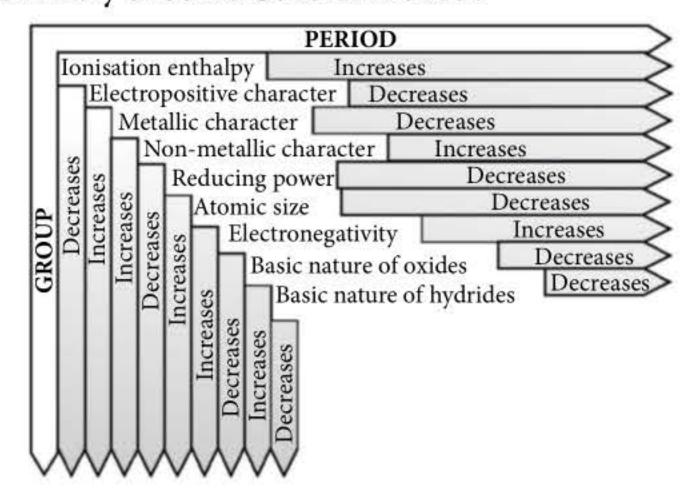
- Factors affecting electron gain enthalpy:
  - Size of the atom :  $\Delta_{eg}H \propto \frac{1}{\text{Size of atom}}$
  - Nuclear charge:  $\Delta_{eg}H \propto \text{Effective nuclear charge}$
  - Screening effect :  $\Delta_{eg}H \propto \frac{1}{\text{Screening effect}}$
- Electron gain enthalpy becomes less negative as we move down a group.
- Electron gain enthalpy becomes more and more negative from left to right in a period (except for noble gases).
- Electronegativity: It is the tendency of an atom to attract the shared pair of electrons towards itself in a covalent bond. Greater the electronegativity of an atom, greater will be its tendency to attract the shared pair of electrons towards itself.
  - Electronegativity decreases on moving down the group and increases along a period.

#### **Periodic Trends in Chemical Properties**

- As we have seen, the ionization enthalpy of the extreme left element in a period is the least and the electron gain enthalpy of the element on the extreme right is the highest negative (excluding noble gases). This results in high chemical reactivity at the two extremes and the lowest in the centre.
- Thus, alkali metals (at extreme left) has maximum tendency to form cation (by loss of an electron) and halogens (at extreme right) has maximum tendency to form anion (by gain of an electron).
- Thus, metallic character is maximum at the left and non-metallic character is maximum at the right within a period.
- The oxides formed by the elements at the left of the periodic table are basic (e.g., Na2O) while oxides formed by the elements at the right of the periodic

- table are acidic (e.g.,  $CL_2O_7$ ). However, oxides of elements in the centre are either amphoteric (e.g.,  $Al_2O_3$ ,  $As_2O_3$ ) or neutral (e.g., CO, NO,  $N_2O$ ).
- In transition metals, change in atomic radii is much smaller than representative elements (*p*-block elements). Their ionization enthalpies are between *s*-and *p*-block elements. Therefore, they are less electropositive than group 1 and 2 metals.

#### **Summary of Some General Trends:**



# PEEP INTO PREVIOUS YEARS

- 4. For the second period elements the correct increasing order of first ionization enthalpy is
  - (a) Li < Be < B < C < O < N < F < Ne
  - (b) Li < Be < B < C < N < O < F < Ne
  - (c) Li < B < Be < C < O < N < F < Ne
  - (d) Li < B < Be < C < N < O < F < Ne

(NEET 2019)

- 5. The correct order of atomic radii in group 13 elements is
  - (a) B < Al < In < Ga < Tl
  - (b) B < Al < Ga < In < Tl
  - (c) B < Ga < Al < Tl < In
  - (d) B < Ga < Al < In < Tl

(NEET 2018)

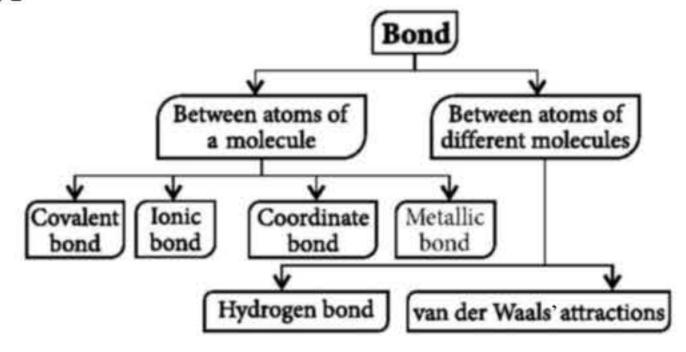
- 6. The option(s) with only amphoteric oxides is (are)
  - (a) Cr<sub>2</sub>O<sub>3</sub>, BeO, SnO, SnO<sub>2</sub>
  - (b) ZnO, Al<sub>2</sub>O<sub>3</sub>, PbO, PbO<sub>2</sub>
  - (c) NO, B<sub>2</sub>O<sub>3</sub>, PbO, SnO<sub>2</sub>
  - (d) Cr<sub>2</sub>O<sub>3</sub>, CrO, SnO, PbO (JEE Advanced 2017)

# Chemical Bonding and Molecular Structure

## CHEMICAL BOND

• The attractive force which holds together the constituent particles (atoms, ions or molecules) in a chemical species is known as *chemical bond*.

#### **Types of Bonds:**



- Covalent Bond: The bond which is formed between two combining atoms by the mutual sharing of electron pair(s) is called *covalent bond*. The compounds containing a covalent bond are called *covalent compounds*.
- **Ionic or Electrovalent Bond :** Ionic bond is a type of chemical bond that involves the electrostatic force of attraction between oppositely charged ions together, is known as *ionic bond* and *electrovalent bond*.

- Octet Rule: The principle of attaining maximum of eight electrons in the valence shell of atom is called octet rule. The octet rule is violated in a significant number of cases:
  - The octet rule does not work in case of atoms which have less than four outer electrons, even if all the outer electrons are used to form bond, an octet cannot be attained.
  - The octet rule does not work in case of atoms which have an extra energy level that may accept electrons and can be used for bonding. For example, PF<sub>3</sub> obeys the octet rule, but PF<sub>5</sub> does not.
  - The octet rule does not work in molecules which have an odd number of electrons, such as NO and ClO<sub>2</sub>, nor does it explain why O<sub>2</sub> is paramagnetic and has two unpaired electrons.
- Formal Charge: The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to the atom in the Lewis structure.
  - Formal charge = Total no. of valence 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).

# PEEP INTO PREVIOUS YEARS

7. Which of the following is the correct electron dot structure of N<sub>2</sub>O molecule?

$$(a) : \ddot{\mathbf{N}} = \mathbf{N} = \ddot{\ddot{\mathbf{O}}}$$

(c) 
$$:N=N=\ddot{O}$$

(a) 
$$: \ddot{N} = N = \ddot{\ddot{O}}$$
 (b)  $: \ddot{N} - N = \ddot{\ddot{O}}$ :  
(c)  $: N = N = \ddot{\ddot{O}}$ :  
(d)  $: N \equiv \dot{N} - \ddot{\ddot{O}}$ :  
(Karnataka CET 2017)

- **8.** The correct statement for the molecule, CsI<sub>3</sub>, is
  - (a) it contains Cs<sup>+</sup>, I<sup>-</sup> and lattice I<sub>2</sub> molecule
  - (b) it is a covalent molecule
  - (c) it contains Cs<sup>+</sup> and I<sub>3</sub> ions
  - (d) it contains  $Cs^{3+}$  and  $I^{-}$  ions. (*JEE Main 2014*)

#### BOND PARAMETERS

The various characteristics features shown by a bond are called the bond parameters

Bond Length: "The average distance between the centres of the nuclei of two bonded atoms in a molecule.

Covalent radius = 
$$r_A + r_B = \frac{d}{2}$$
 [if  $r_A = r_B$ ]

- **Bond Enthalpy**: The amount of energy (in kJ mol<sup>-1</sup>) required to break one mole of bond of a particular type between two atoms to separate them in gaseous state.
- Bond Angle: The angle between the lines representing the directions of the bond. *i.e.*, orbital containing the bonding electrons is called bond angle.
- Bond Order: The bond order is given by the number of bonds between the two atoms in a molecule. e.g., Bond order in  $H_2$  is one, in  $O_2$  it is two and in  $N_2$  it is three.
  - Isoelectronic molecules and ions have identical bond order. For example  $F_2$  and  $O_2^{2-}$  have bond order 1 and N<sub>2</sub>, CO and NO<sup>+</sup> have bond order 3.
  - The stabilities of molecules can be understood by the statement "With increase in bond order, bond enthalpy increases and bond length decrease."

#### **Polarity of Bond:**

Dipole moment  $(\mu)$  = Charge (q) × Distance of separation (d)

It is usually expressed in Debye (D).

SI unit of dipole moment is Cm.  $1 D = 3.335 \times 10^{-30} Cm$ .

Percent ionic character

$$= \frac{\text{Actual dipole moment of the bond}}{\text{Dipole moment of a pure}} \times 100$$
ionic bond

% ionic character can also be calculated by using,

Pauling equation =  $18(\chi_A - \chi_B)^{1.4}$ 

Hannay and Smith equation

$$= 16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2$$

Fajan's Rule: The power of an ion (cation) to distort the electronic cloud of other ion (anion) is known as its polarising or polarisation power, whereas the tendency of an ion (anion) to get polarised by other ion is known as its polarisability. Higher the degree of ionic polarisation greater is the covalent character.

- Polarising power 
$$\propto \frac{1}{\text{size of cation}}$$

- Polarisability of anion ∞ size of anion
- Covalent character ∝ size of anion

$$\frac{1}{\text{size of cation}}$$
  $\propto$  charge on anion and cation

#### **Relation between Bond Parameters:**

- Bond length 
$$\infty$$
 size of atom  $\infty$   $\frac{1}{\% s\text{-character}}$ 
 $\infty$   $\frac{1}{\text{bond multiplicity}}$ 

- Bond energy 
$$\propto \frac{1}{\text{bond length}}$$

$$\infty$$
% s-character  $\infty \frac{1}{\text{no. of lone pairs}}$ 

Bond angle  $\propto$  % *s*-character

∞ electronegativity of central atom

# Valence Shell Electron Pair Repulsion (VSEPR) Theory

Bonded atoms in a molecule adopt that particular arrangement in space around the central atom which keeps them on the average as far as possible so that there are no further repulsions between them. As a result, molecule has minimum energy and maximum stability.

#### Postulates of VSEPR theory are:

- The shape of molecules can be determined by the number of electron pairs (bonding as well as non-bonding) in the valence shell of the central atom.
- Electron pairs in the valence shell repel one another and the order of repulsion is : lp - lp > lp - bp > bp - bp

- Electron pairs tend to occupy such positions in space that minimise repulsion and maximise distance between them.
- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

# PEEP INTO PREVIOUS YEARS

- 9. Consider the following species: CN<sup>+</sup>, CN<sup>-</sup>, NO and CN. Which one of these will have the highest bond order?
  - (a) NO
- (b) CN
- (c) CN<sup>+</sup>
- (d) CN

(NEET 2018)

- 10. Predict the correct order among the following:
  - (a) bond pair bond pair > lone pair bond pair

> lone pair - lone pair

- (b) lone pair bond pair > bond pair bond pair > lone pair lone pair
- (c) lone pair lone pair > lone pair bond pair > bond pair bond pair
- (d) lone pair lone pair > bond pair bond pair > lone pair bond pair (NEET-I 2016)

## VALENCE BOND THEORY (VBT)

- According to V.B.T., a covalent bond is formed between the two atoms by the overlap of half filled valence atomic orbitals of each atom containing one unpaired electron.
- The bond is formed when atoms approach each other in such a way that occupied orbitals with similar energies are able to overlap.
- Greater the overlap, stronger is the bond.

#### Types of Overlapping and Nature of Covalent Bonds:

- Sigma (σ) Bond: This type of covalent bond is formed by the end to end overlapping of bonding orbitals along the internuclear axis. The overlap is known as head on overlap or axial overlap.
- **Pi** (π) **Bond**: This type of covalent bond is formed by the sidewise overlap of the half-filled atomic orbitals of bonding atoms. Such an overlap is known as sidewise or lateral overlap. The atomic orbitals overlap in such a way that their axis remain parallel to each other and perpendicular to the internuclear axis.
- During the formation of a  $\pi$ -bond, the overlapping occur to a smaller extent. Therefore, a  $\sigma$ -bond is stronger than a  $\pi$ -bond.

#### **Hybridisation**

- The process of mixing of atomic orbitals of nearly same energy to produce a set of entirely new orbitals of equivalent energy is known as hybridisation. The new orbitals thus formed are known as hybrid orbitals.
- Some Important Conditions for Hybridisation :
  - The orbitals present in the valence shell of the atom are hybridised.
  - Orbitals undergoing hybridisation should have nearly same energies.
  - Promotion of electron is not essential before hybridisation occurs.

#### Salient Features of Hybridisation :

- The number of hybrid orbitals are equal to the number of the atomic orbitals that get hybridised.
- The hybridised orbitals are always equivalent in energies and shapes.
- The hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between the electron pairs.
- Hybridisation =  $\frac{1}{2}(V + M C + A)$

where, H = no. of orbitals involved in hybridisation viz. 2, 3, 4, 5, 6 and 7, hence nature of hybridisation will be sp,  $sp^2$ ,  $sp^3$ ,  $sp^3d$ ,  $sp^3d^2$ ,  $sp^3d^3$  respectively.

 $V = \text{no. of } e^- \text{ in valence shell of the central atom,}$ 

M = no. of monovalent atom,

C = charge on cation

A =charge on anion

# MOLECULAR ORBITAL THEORY OR LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

- Molecular orbital theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features of this theory are:
- Molecular orbitals are formed by the addition or subtraction of wave functions of the atomic orbitals.
- Addition of wave functions during overlap of atomic orbitals leads to formation of bonding molecular orbitals with lower energy, they can be σ or π.
- Subtraction of wave functions during overlap of atomic orbitals leads to formation of anti-bonding molecular orbitals with higher energy, written as σ\* or π\*.
- Filling of electrons in molecular orbitals takes place in accordance with aufbau's principle, Hund's rule and Pauli's exclusion principle.

Energy order for molecular orbitals up to  $N_2$ :

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z$$
  
 $< (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$ 

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: The number of covalent bonds formed in a molecule is called its bond order. Mathematically, it is defined as half of the difference between the number of bonding and anti-bonding electrons.

Bond order (B.O.) = 
$$\frac{1}{2} (N_b - N_a)$$

where,  $N_b$  is number of electrons present in bonding molecular orbitals and  $N_a$  is number of electrons present in anti bonding molecular orbitals.

- 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.

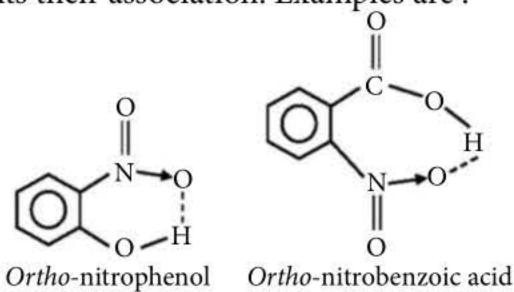
# HYDROGEN BONDING

When hydrogen atom is bonded to atoms of highly electronegative elements such as fluorine, oxygen or nitrogen, the Hydrogen atom forms a weak bond with the electronegative atom of the other molecule. This weak bond is called hydrogen bond. For example, hydrogen fluoride, HF,

$$--H$$
 $\stackrel{\delta_{+}}{---}F$  $\stackrel{\delta_{-}}{---}H$  $\stackrel{\delta_{+}}{---}F$  $\stackrel{\delta_{-}}{----}H$  $\stackrel{\delta_{-}}{----}F$  $\stackrel{\delta_{-}}{----}H$ 

#### Types of Hydrogen Bonding

- Intermolecular hydrogen bonding: Formed between different molecules of the same or different substances.
  - Example: HF, H<sub>2</sub>O, ROH (same compound) and hydrogen bonding between water and alcohol, or water and ammonia (different compounds), etc.
- Intramolecular hydrogen bonding: Hydrogen bond is formed between the hydrogen atom and the highly electronegative atom (F, O or N) present in the same molecule. Intramolecular hydrogen bond results in the cyclization of the molecule and prevents their association. Examples are:



# PEEP INTO PREVIOUS YEARS

- 11. The type of hybridisation and number of lone pair(s) of electrons of Xe in XeOF<sub>4</sub>, respectively, are
  - (a)  $sp^3d$  and 2
- (b)  $sp^3d^2$  and 2
  - (c)  $sp^3d^2$  and 1 (d)  $sp^3d$  and 1

(JEE Main 2019)

- 12. Which one of the following compounds shows the presence of intramolecular hydrogen bond?
  - (a)  $H_2O_2$
  - (b) HCN
  - (c) Cellulose
  - (d) Concentrated acetic acid

(NEET-II 2016)

(a,b)

# **Answer Key For Peep Into Previous Years**

- 1.
- **(b)**

- **(b)**

# WRAPitUP

- In which of the following arrangements, the order is not according to the property indicated?
  - (a)  $Al^{3+} < Mg^{2+} < Na^+ < F^-$  (Increasing ionic size)
  - (b) B < C < N < O (Increasing first ionisation energy)
- (c) I < Br < F < Cl (Increasing electron gain enthalpy)
- (d) Li < Na < K < Rb (Increasing metallic radius)
- 2. In which of the following species the underlined C-atom has  $sp^3$  hybridization?