THE PEARSON GUIDE TO

INORGANIC CHEMISTRY FOR THE IIT JEE

Atul Singhal

2012

ALWAYS LEARNING

PEARSON

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Contents

Preface to the Current Edition

The response to the first edition of the book and positive feedback from teachers and students has motivated me to work upon this revised and thoroughly pruned edition.

It is now power-packed with new questions of the latest IIT-JEE format. I hope that students will find this book useful. All the best!

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Preface

The Pearson Guide to Inorganic Chemistry for the IIT JEE is an invaluable book for all the students preparing for the prestigious engineering entrance examination. It provides class-tested course material and problems that will supplement any kind of coaching or resource the students might be using. Because of its comprehensive and in-depth approach, it will be especially helpful for those students who do not have enough time or money to take classroom courses.

- A careful scrutiny of previous years' IIT papers and various other competitive examinations during the last 10 to 12 years was made before writing this book. It is strictly based on the latest IIT syllabus (2009–10) recommended by the executive board. It covers the subject in a structured way and familiarizes students with the trends in these examinations. Not many books in the market can stand up to this material when it comes to the strict alignment with the prescribed syllabus.
- It is written in a lucid manner to assist students to understand the concepts without the help of any guide.
- The objective of this book is to provide this vast subject in a structured and useful manner so as to familiarize the candidates taking the current examinations with the current trends and types of multiple-choice questions asked.
- The multiple-choice questions have been arranged in following categories:

Straight Objective Type Questions (Single Choice), Brainteasers Objective Type Questions (Single Choice), Multiple Correct Answer Type Questions (More than one choice), Linked-Comprehension Type Questions, Assertion and Reasoning Questions, Matrix-Match Type Questions and the IIT JEE Corner.

This book is written to pass on to another generation, my fascination with descriptive inorganic chemistry. Thus, the comments of the readers, both students and instructors, will be sincerely appreciated. Any suggestions for added or updated additional readings would also be welcome.

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1

CHEMICAL BONDING

Chapter Contents

Orbital overlap and covalent bond; Hybridization involving s, p and d orbitals only; Orbital energy diagrams for homonuclear diatomic species; Hydrogen bond; Polarity in molecules, dipole moment (qualitative aspects only); VSEPR model and shapes of molecules (linear, angular, triangular, square planar, pyramidal, square pyramidal, trigonal bipyramidal, tetrahedral and octahedral) and various levels of multiple-choice questions.

CHEMICAL BOND

Chemical bond is the force of attraction that binds two atoms together. A chemical bond balances the force of attraction and force of repulsion at a particular distance.

A chemical bond is formed to:

- attain the octet state
- minimize energy
- gain stability
- decrease reactivity

When two atoms come close to each other, forces of attraction and repulsion operate between them. The distance at which the attractive forces overcome repulsive forces is called bond distance. Here, the potential energy for the system is lowest, hence the bond is formed.

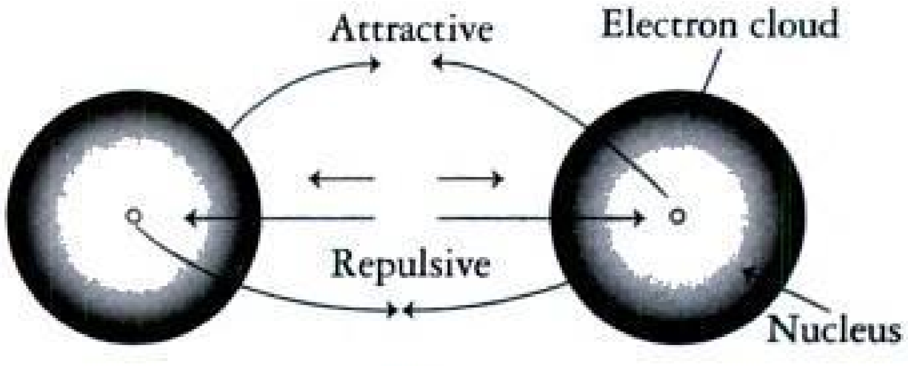

Fig. 1.1

Types of Bonds

Following are the six types of chemical bonds. Here, they are listed in the decreasing order of their respective bond strengths.

1. Ionic bond
2. Covalent bond
3. Coordinate bond
4. Metallic bond
5. Hydrogen bond
6. van der Waals bond

Metallic bond, hydrogen bond and van der Waals bond are interactions.

Octet Rule

It was introduced by Lewis and Kossel. According to this rule, each atom tries to obtain the octet state, that is, a state with eight valence electrons.

Exceptions to the octet rule

- Transition metal ions like Cr^{3+}, Mn^{2+}, Fe^{2+}.
- Pseudo inert gas configuration cations like Zn^{2+}, Cd^{2+}.

Contraction of octet state

- Here, the central atom is electron deficient or does not have an octet state. For example,

BeX_2	BX_3	AlX_3	$Ge(CH_3)_3$
4	6	6	$6e^-$

Expansion of octet state

- Here, the central atom has more than 8 electrons due to empty d-orbitals. For example, PCl_5, SF_6, OsF_8, ICl_3 etc

PCl_5	SF_6	OsF_8	ICl_3 etc.
10	12	16	$10e^-$

- Odd electronic species like NO, NO_2, ClO_2.
- Interhalogens compounds like IF_7, BrF_3.
- Compounds of xenon such as XeF_2, XeF_4, XeF_6.

IONIC OR KERNEL BOND

An Ionic bond is formed by the complete transfer of valence electrons from a metal to a non-metal. This was first studied by Kossel.

For example,

$$\underset{(2,8,1)}{Na} + \underset{(2,8,7)}{Cl} \longrightarrow \underset{(2,8)}{Na^+}\ \underset{(2,8)}{Cl^-}$$

$$\underset{(2,8,2)}{Mg} + \underset{(2,6)}{O} \longrightarrow \underset{(2,8)}{Mg^{+2}}\ \underset{(2,8)}{O^{-2}}$$

$$\underset{(2,8,3)}{Al} + \underset{(2,5)}{N} \longrightarrow \underset{(2,8)}{Al^{+3}}\ \underset{(2,8)}{N^{-3}}$$

- Number of electrons transferred is equal to electrovalency.
- Maximum number of electrons transferred by a metal to non-metal is three, as in the case with AlF_3, (Al metal transfers three electrons to F).
- During electron transfer, the outermost orbit of metal is destroyed. The remaining portion is called core or kernel, hence this bond is also called kernel bond.
- Nature of ionic bond is electrostatic or coloumbic force of attraction.
- It is a non-directional bond.

Conditions for the Formation of an Ionic Bond

The process of bond formation is exothermic where $\Delta H = -Ve$. The essential conditions include

- Metal must have low ionization energy.
- Non-metals must have high electron affinity.
- Ions must have high lattice energy.
- Cation should be large with low electronegativity.
- Anion must be small with high electronegativity.

Born–Haber Cycle

The formation of an ionic compound in terms of energy can be shown by Born–Haber cycle. It is also used to find lattice energy, ionization energy and electron affinity.

For example,

$$M(s) \xrightarrow[+S]{\text{Sublimation}} M(g) \xrightarrow[+I]{\text{Ionization}} M^+(g) + e^-$$

$$\tfrac{1}{2} X_2 \xrightarrow[+1/2\,D]{\text{Decomposition}} X(g) \xrightarrow[-E]{\text{Addition of } e^-} X^-(g)$$

$$M^+_{(g)} + X^-(g) \xrightarrow[-U]{\text{Crystal formation}} MX(g)$$

$$\Delta H_f = S + \tfrac{1}{2} D + I - E - U$$

Here,

S = Heat of sublimation
D = Heat of dissociation
I = Ionization enthalpy
E = Electron gain enthalpy or electron affinity
U = Lattice energy

Types of Overlapping

1. **s-s Overlapping:** Overlapping between s-s electrons of two similar or dissimilar atoms is called s-s overlapping and forms a single covalent bond.

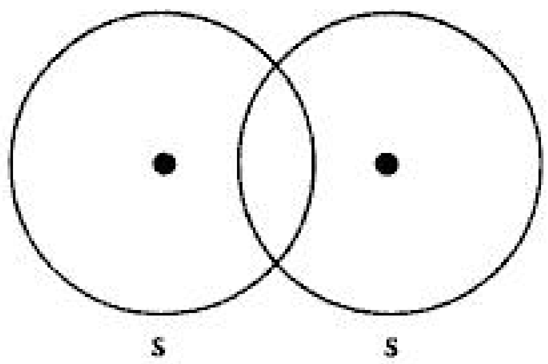

Fig. 1.3 Formation of hydrogen molecule by s-s overlapping.

2. **s-p Overlapping:** Overlapping between s and p electrons is called s-p overlapping. NH_3 is formed by the overlapping between three electrons of nitrogen (px, py and pz) with three electrons of three hydrogen atoms.

   $_7N = 1s^2, 2s^2, 2px^1\ py^1\ pz^1$

   $_1H = 1s^1$

   Strong bond can be formed only when hydrogen electrons approach in the direction of X, Y and Z axis at right angles to each other.

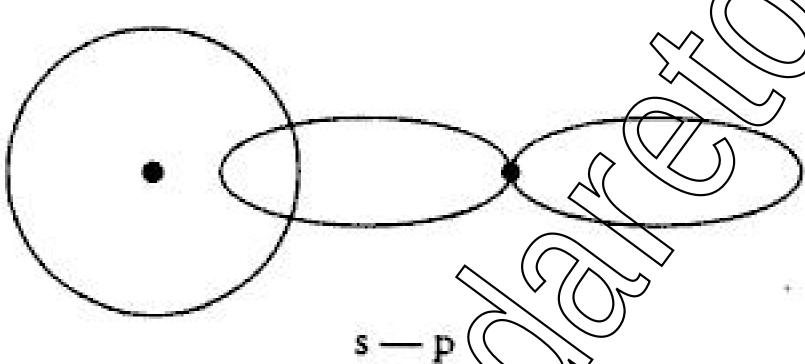

Fig. 1.4

3. **p-p Overlapping:** p-p overlapping is formed by the overlapping of the p-orbitals of the atoms. In case of chlorine molecule, it is formed by the overlapping of the 3pz orbitals of two chlorine atoms.

   $_{17}Cl = 1s^2, 2s^2\ 2p^6, 3s^2, 3px^2, 3py^2, 3pz^1$

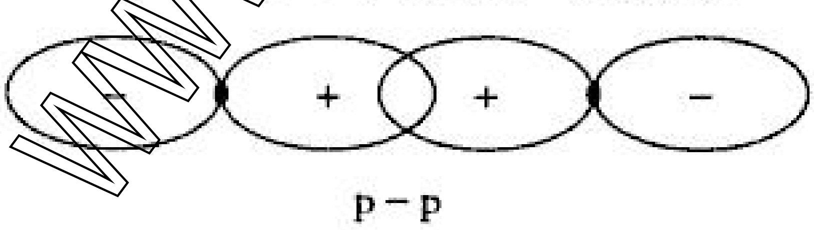

Fig. 1.5

Some Important Features of Bond

Bond Length

- Bond length is the average distance between the centers of the nuclei of the two bonded atoms.
- It is determined by X-ray diffraction and spectroscopic methods.
- In case of ionic compounds, it is the sum of ionic radius of cation and anion, while in case of covalent compounds, it is sum of their covalent radius.

Factors affecting bond length

- Bond length ∝ Size of atom. For example,

  HF < HCl < HBr < HI
  (Atomic size)

  Since F < Cl < Br < I

- Bond length $\propto \frac{1}{\text{Bond order or multiplicity}}$

  For example, C – C > C = C > C ≡ C
  1.54Å 1.34Å 1.32Å

- Bond length $\propto \frac{1}{s\%}$

that is,	sp^3	>	sp^2	>	sp
s%	25%		33%		50%

- Bond length ∝ Electronic repulsion
  For example, $H_2^- > H_2^+$
- Resonance and hyperconjugation also change bond length.
  For example, in benzene, C – C bond length is 1.39 Å, that is, in between C – C and C=C.

Bond Energy

- It is the energy needed to break one mole of bond of a particular type, so as to separate them into gaseous atoms. It is also called bond dissociation energy.
- Bond energy can also be defined as the energy released during the formation of one mole of a particular bond.

Factors affecting bond energy

- Bond energy ∝ Bond order or multiplicity
  For example, C ≡ C > C = C > C – C

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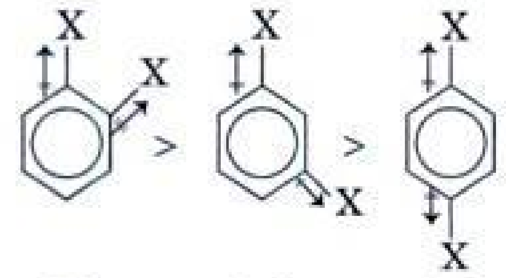
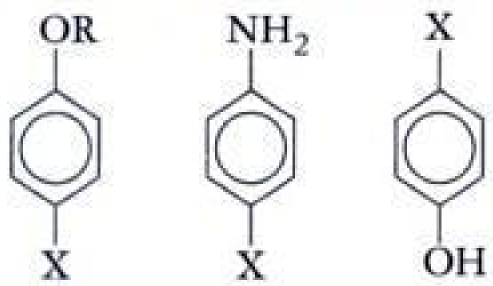
For example,



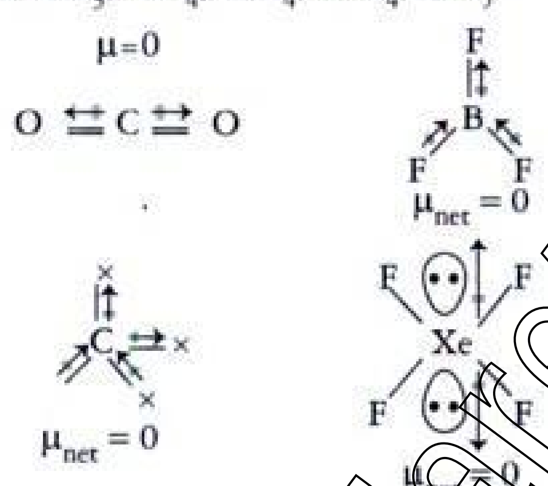
'o' 'm' 'p'

60° 120° 180°

In case of para forms M μ_{net} is positive if both the species are different. For example,



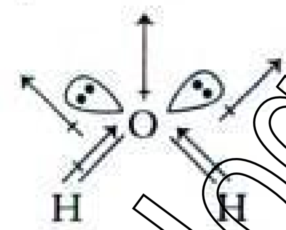
- Homoatomic molecules like X_2, N_2, O_2 and molecules having normal shapes according to hybridization like linear, trigonal, tetrahedral will be non-polar, as for them, the dipole moment is zero. For example, BX_3, CH_4, CCl_4, $SiCl_4$, PCl_5.



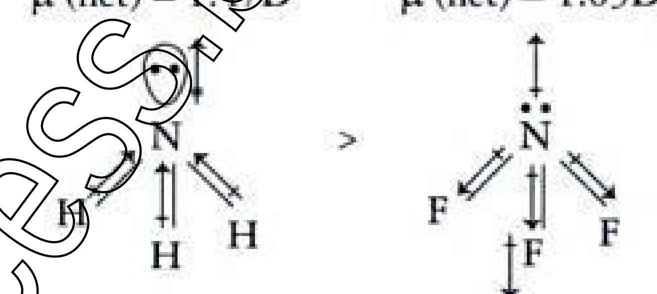
Here, μ (net) = 0 as C = O bonds are in opposing directions.

- Molecules in which the central atom has lone pair of electrons or have distorted shapes, like angular, pyramidal, sea-saw shapes will have some value of dipole moment and will be polar in nature. For example, H_2O, H_2S, OF_2, NH_3, PH_3, PCl_3, SCl_4, SO_2, $SnCl_2$ etc.

μ(net) = 1.82D



μ (net) = 1.47D μ (net) = 1.03D



Ammonia has more dipole moment than NF_3 as in ammonia μ (net) is in the direction of lone pair electrons i.e., it is additive while in NF_3 μ (net) is opposite to lone pair i.e., substractive.

- Dipole moment of a cis-alkene is more than trans-alkene. In trans-alkenes, it is zero due to symmetry in most of the cases.

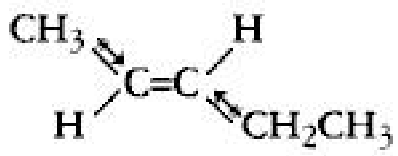
Dipole Moment of Some Common Molecules

Molecule	H_2	N_2	CH_4	Cl_2	CS_2	C_2H_2	CH_2F_2	O_2	O_3	C_2H_6	SO_2	CO	CsI	NaCl	CH_3OH	C_2H_5OH	H_2O	HF
Dipole moment	0	0	0	0	0	0	1.96D	0	0.52D	0	1.61D	1.12	12.1	8.3	1.69	1.67D	1.84	1.91
Molecule	HCl	NH_3	N_2O	H_2S	H_2O_2	NF_3	$CHCl_3$	PH_3	HCN	$SbCl_3$	CH_3Cl	S_8	PCl_5		Trans-butene	IF_7	PX_5	CX_4
Dipole moment	1.02	1.46	0.17	0.92	1.84	0.55	1.15	0.58	2.93	3.9	1.86	0	0	0	0	0	0	0

cis-but-2-ene trans-but-2-ene

Exception: Unsymmetric alkenes with odd number of carbon atoms have some value of dipole moment.

For example, trans-2-pentene



Specific cases of dipole moment

→ $CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$
Highly polar Non-polar

→ $CH_3Cl > CH_3F > CH_3Br > CH_3I$

Uses

- To find geometry of a complex/molecule etc.
- To find ionic character or nature in a covalent species.

Ionic nature % = $\dfrac{\mu_{observed}}{\mu_{calculated}\,(q \times r)} \times 100$

- To distinguish between –cis and –trans alkenes

Cis-but 2-ene > trans but-2-ene
μ=+ve μ=0

Illustrations

1. **The experimentally determined dipole moment of KF is 2.87×10^{-29} cm. The distance between the centers of charge in a KF dipole is 2.66×10^{-10} m. Calculate the percentage ionic character of KF.**

Solution

$\mu = e \times d$ coulombs meter

For KF = 2.66×10^{-10} m

For complete separation of a unit charge (electronic charge), $e = 1.602 \times 10^{-19}$ C

$\mu = 1.602 \times 10^{-19} \times 2.66 \times 10^{-10}$

$= 4.26 \times 10^{-29}$ cm

% ionic character a KCl

$= \dfrac{2.87 \times 10^{-29}}{4.26 \times 10^{-29}} \times 100$

$= 67.4$ %.

2. The dipole moment of KCl is 3.336×10^{-29} coulomb meter which indicates that it is a highly polar molecule. The interatomic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. Calculate the dipole moment of KCl molecule if there were opposite charges of one fundamental unit located at each nucleus. Calculate the percentage ionic character of KCl.

Solution

$\mu = e \times d$ coulombs meter

For KCl d = 2.6×10^{-10} m

For complete separation of unit charge (electronic charge), $e = 1.602 \times 10^{-19}$ C

$\mu = 1.602 \times 10^{-19} \times 2.6 \times 10^{-10}$

$= 4.1652 \times 10^{-29}$ cm

μ (KCl) = 3.336×10^{-29} cm

Per cent ionic character of KCl

$= \dfrac{3.336 \times 10^{-29}}{4.1652 \times 10^{-29}} \times 100$

$= 80.09$ %

SIGMA AND PI BONDS

Sigma (σ) Bond

Sigma bond is formed by axial or headtohead or linear overlapping between two s–s or s–p or p–p orbitals.

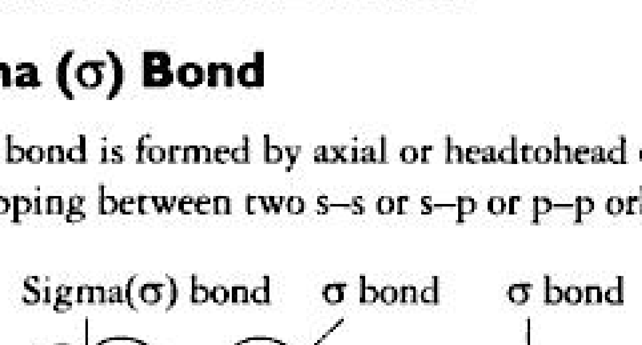


Fig. 1.1

1. Sigma bond is stronger and therefore less reactive, due to more effective and stronger overlapping than □ bond.
2. The minimum and maximum number of □ bonds between two bonded atoms is 1.
3. Stability □ Number of sigma bonds.

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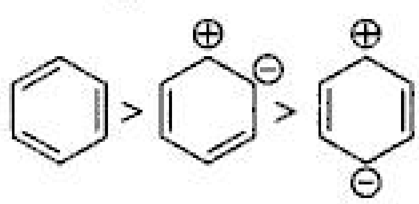
although it has double bonds (due to delocalization of π electrons or resonance).

- Benzene has 36 kcal/mole of resonance energy.
- Resonance energy of CO_2 is 154.9 kJ.
- In tautomerism, arrangement of atoms is different for its different arrangements but in resonance, the arrangement of atoms is the same.

Stability of Different Canonical Structures

1. A non-polar structure is always more stable than a polar structure. In the following example, the structures are arranged in a decreasing order of stability.



In the last two structures the charges are apart so they are less stable.

2. Greater the number of covalent bonds greater will be the stability. Therefore,

$$CH_3-C\equiv\overset{\oplus}{O} > CH_3-\overset{+}{C}=O$$

3. The canonical structure in which positive charge in an electro+positive atom and negative charge on the electro–negative atom is more stable. Therefore,

4. The canonical structure in which each atom has an octet state is more stable. Therefore,

$$\underset{8e^-}{CH_3-C\equiv\overset{\oplus}{O}} > \underset{6e^-}{CH_3-\overset{\oplus}{C}=O}$$

5. If like charges are closer then the structure will be unstable.

$$:\ddot{N}=\overset{+}{N}=O \longleftrightarrow N\equiv\overset{+}{N}-\ddot{O}:^- \longleftrightarrow :\ddot{N}-\overset{\oplus}{N}=\overset{\oplus}{O}$$

Most stable Unstable

Types of Resonance

1. **Isovalent resonance** The canonical structures havesamenumberofbondsandsametypeofcharges. For example, SO_2, NO_2, CO_3^{-2}
2. **Heterovalent resonance** Here, the canonical structures have different number of bonds and charges. For example, buta- 1, 3-diene, vinyl cyanide.

Resonance and Bond Order

$$\text{Bond order} = \frac{\text{Total no. of order between two atoms}}{\text{Total no. of major canonical structures}}$$

Example, In SO_3, B.O. = 4/3 = 1.33

In ClO_4^-, B.O. = 7/4 = 1.75

HYBRIDIZATION

- Pauling and Slater introduced this concept to explain the shape of molecules which could not be explained by the valence bond theory.
- It is the intermixing or re-distribution of energy among two or more half-filled, fully filled, incompletely filled or empty orbitals of comparable energy, to form same number of hybrid orbitals. Hybrids have identical energies and similar shapes.

Facts About Hybridization

- Number of atomic orbitals taking part in hybridization is equal to number of hybrids formed.
- Electrons do not undergo hybridization.
- A hybrid bond is always a sigma bond.
- A hybrid bond is always stronger than a non-hybrid bond.
- Hybridization occurs at the time of bond formation.
- Hybridization □ Overlapping (for enough overlapping, orbitals must be at an approppriate distance from each other, that is, neither very close nor very far).
- Hybridization increases stability and decreases reactivity and energy of a molecule.
- Hybridization occurs in the central atom in a molecule (NH_3, H_2O, CH_4). Here, the central atoms are N, O, C respectively.
- Hybridization does not occur in isolated atoms but in bonded atoms.

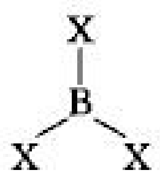
Types of Hybridization

1. **sp hybridization:** Here, one s and one p orbitals form two sp hybrid orbitals after intermixing.
   - Shape of molecule is linear and bond angle is 180°. For example, X–M–X (Mg, Be, Zn, Hg)

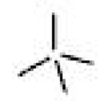
     $$\underset{sp}{H - C} \equiv \underset{sp}{C - H}$$

   Some other examples are CO_2, and CS_2.

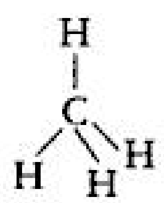
2. **sp^2 hybridization:** Here, one s and two p orbitals intermix to form three new sp^2 hybrid orbitals.
   - Shape of these species is trigonal or coplanar and the bond angle is 120°. For example,



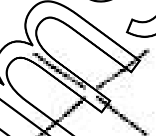
3. **sp^3 hybridization:** Here, one s and three p orbitals intermix to give four new sp^3 hybrid orbitals.



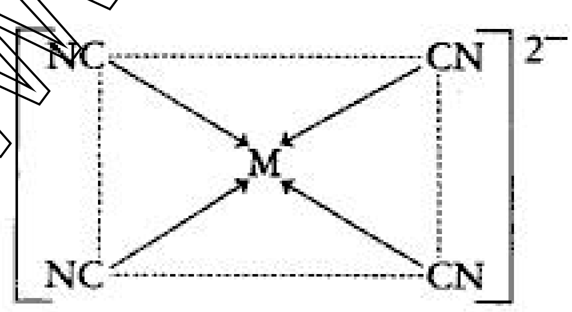
   - Shape of the species is tetrahedral and bond angle is 109° 28′. For example, C_2H_6, CX_4, SiX_4, NH_4^+, BX_4^-, NH_3, PH_3, H_2O, H_2S.



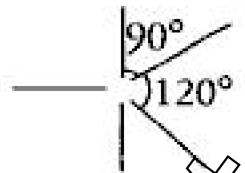
4. **dsp^2 hybridization:** Here, one s, two p and one d orbitals ($d_{x^2-y^2}$) intermix to give four new dsp^2 hybrid orbitals.



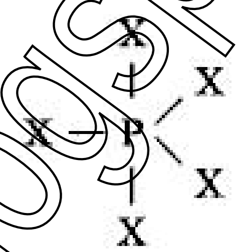
   - Shape of the species is square planar and bond angle is 90°. For example, $[Ni(CN)_4]^{-2}$, $[Cu(CN)_4]^{2-}$



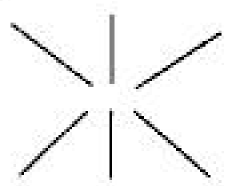
5. **sp^3d hybridization:** Here, one s, three p and one d-orbital (dz^2) intermix to form five new sp^3d hybrid orbitals.



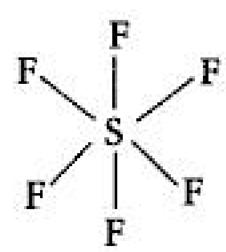
   - Shape of the species is trigonal bipyramidal and bond angles are 90°, 120°. For example, PX_5, XeF_2, I_3^-



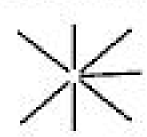
6. **sp^3d^2 hybridization:** Here, one s, three p and two d-orbital ($d_z{}^2$ and $d_{x^2-y^2}$) intermix to form six new sp^3d^2 hybrid orbitals.



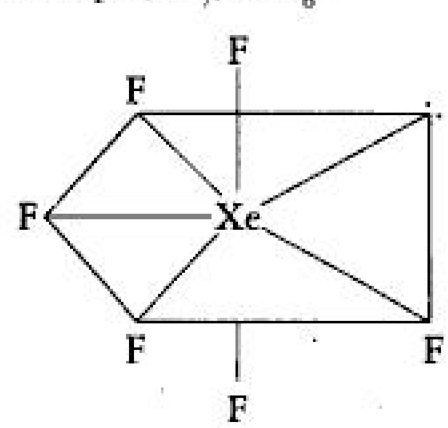
   - Shape of the species is octahedral and bond angle is 90°. For example, SF_6, XeF_4.



7. **sp^3d^3 hybridization:** Here one s, three p and three d orbital (d_{xy}, d_{yz}, d_{xz}) intermix to form seven new sp^3d^3 hybrid orbitals.



   - Shape of the species is pentagonal bipyramidal and bond angle is between 72° to 90°. For example, IF_7, XeF_6.



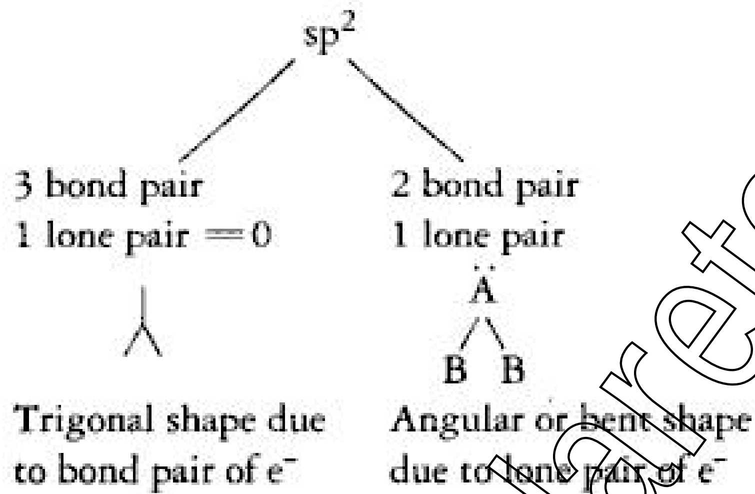
- According to this theory, besides hybridization, the nature of electrons around the central atom also decide the shape of molecule.
- There may be two types of electrons around the central atom, that is, bond pair or lone pair of electrons.
- These electrons undergo electron–electron repulsion and the decreasing order of electronic repulsion follows lp–lp > lp–bp > bp–bp.
- Due to this electronic repulsion, the shape of the molecule becomes distorted and the bond angle changes.

  Distortion in shape $\propto$ e^-–e^- repulsion

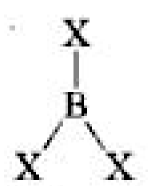
  Distortion in shape or change in bond angle $\propto$ electronic repulsion.

Geometry of Some Molecules and Ions

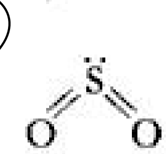
sp^2 hybridization



For example, BX_3, BH_3, SO_2



Normal trigonal shape

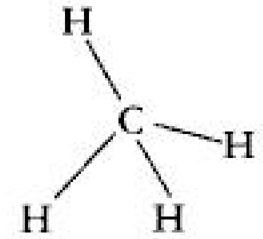


Bent shape

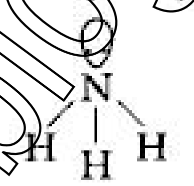
Here, S atom has two bond pairs and one lone pair of electron, so lp–bp type of repulsion distorts the shape, that is, it bends and changes the bond angle and the shape becomes angular. Same holds true for $SnCl_2$ and $PbCl_2$.

sp^3 hybridization

1. When the central atom has four bond pairs of electrons, the shape will be normal with normal bond angle of 109° 28' which The Shape tetrahedral. For example, CH_4, CCl_4, $SiCl_4$, NH_4^+, BX_4^-

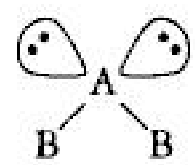


2. When the central atom has 3 bond pairs and 1 lone pair of electron, there will be lp–bp type of repulsion, which distorts the shape and changes the bond angle, that is, the shape becomes pyramidal and the bond angles are less than 109° 28' For example, NH_3, PH_3, NX_3, PX_3



In ammonia, the bond angle is 107°.

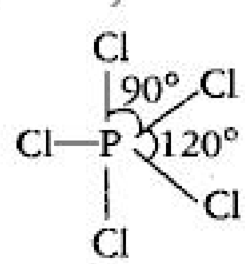
3. When the central atom has 2 lone pair and 2 bond pair of electron, there will be lp–lp type of electronic repulsion, hence the shape will be distorted and it will be angular or bent. For example, H_2O, H_2S, OF_2, SCl_2



4. When the central atom has 3 lone pairs and 1 bond pair of electrons, there will be lp–lp type of electronic repulsion. hence, shape is highly distorted and it becomes linear. For example, I–Cl, HCl

sp^3d hybridization

1. When the central atom has 5 bond pair of electrons, the shape will be normal with normal bond angle, that is, the shape becomes trigonal bipyramidal and bond angle of 90° and 120°. As only bp–bp type of electronic repulsion occurs, hence there is no distortion in shape and no change in bond angle. For example, PCl_5, AsF_5 and PF_5.



Due to the difference in bond angles here bond length also varies far axial and equitorial bonds.

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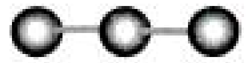
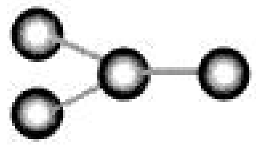
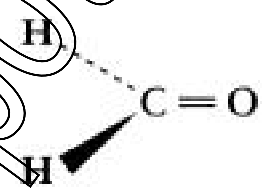
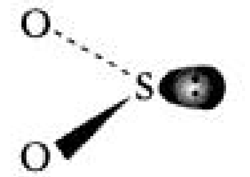
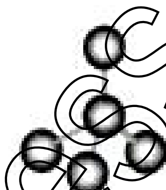
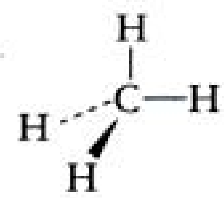
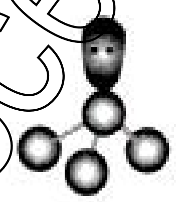
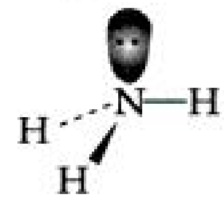
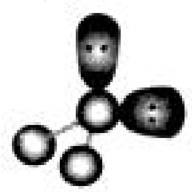
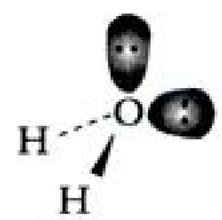
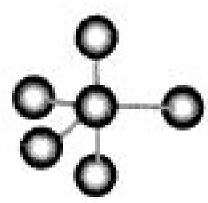
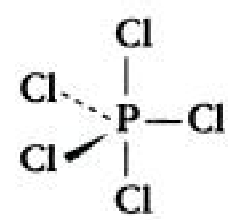
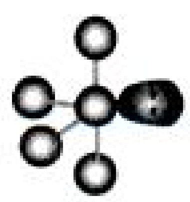
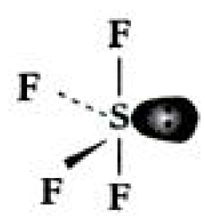
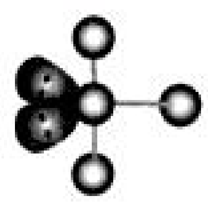
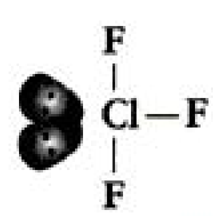
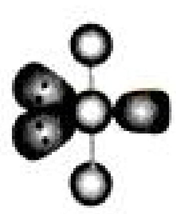
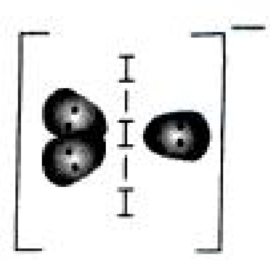
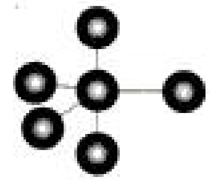
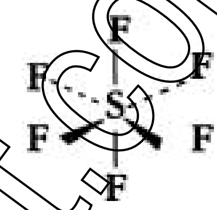
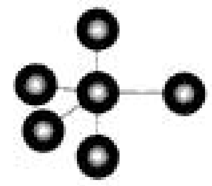
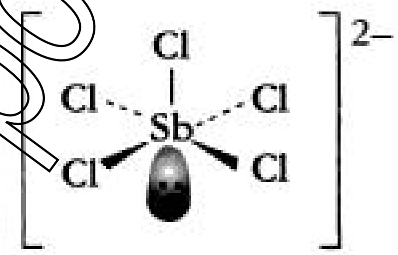
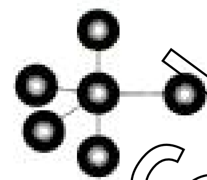
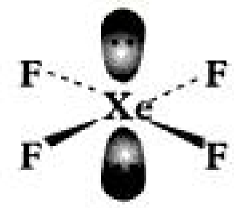
Hybridization and Shapes of Some Simple Molecules

Number of Bonds	Number of Lone Pairs	Number of Charge Clouds	Molecular Geometry and Shape		Examples
2	0	2		Linear	O=C=O
3	0	3		Trigonal planar	
2	1			Bent	
4	0	4		Tetrahedral	
3	1			Trigonal pyramidal	
2	2			Bent	
5	0	5		Trigonal bipyramidal	
4	1			See-saw	
3	2			T-shaped	
2	3			Linear	

Number of Bonds	Number of Lone Pairs	Number of Charge Clouds	Molecular Geometry and Shape	Examples
6	0	6	 Octahedral	
5	1	6	 Square Pyramidal	
4	2	6	 Square Planar	

3. Atomic orbitals must have same symmetry along with the major molecular axis, for example, if Z axis is the main molecular axis, then only p_z–p_z orbitals will overlap and not p_x or p_y.

- Molecular orbitals are formed due to constructive and destructive interference of atomic orbitals.
- Constructive interaction of orbitals between orbital lobes having same wave function ψ produces bonding molecular orbitals like σ, π and Δ. These are HoMOs (Highest Occupied Molecular Orbitals).

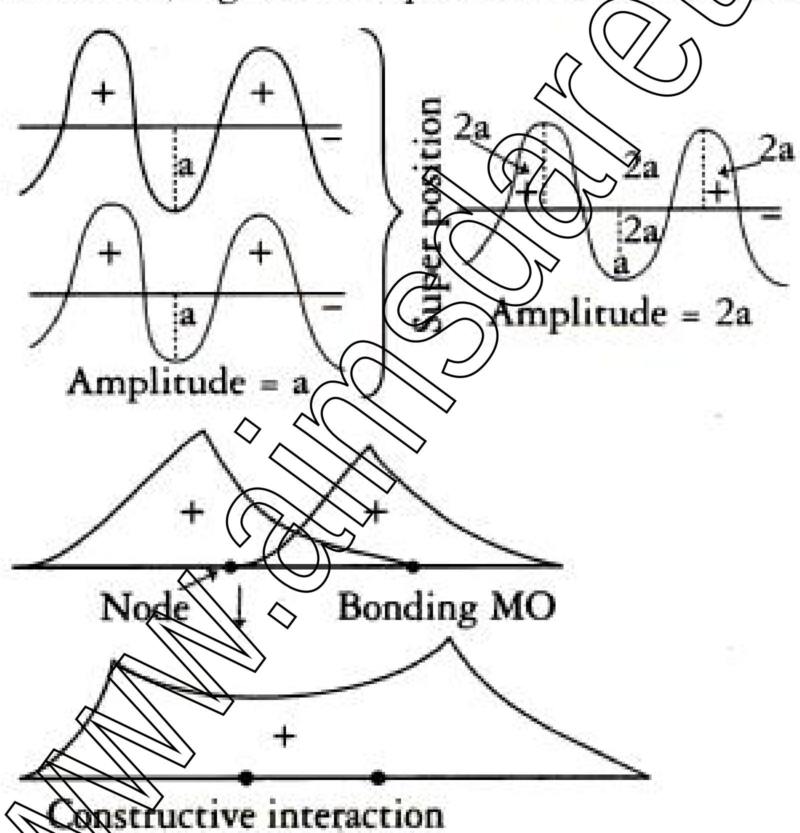


Fig. 1.13

- Destructive interaction between orbitals having different sign of c produces anti-bonding molecular orbitals or LuMOs (Lowest Unoccupied Molecular Orbitals). For example, σ*, π*, d*.

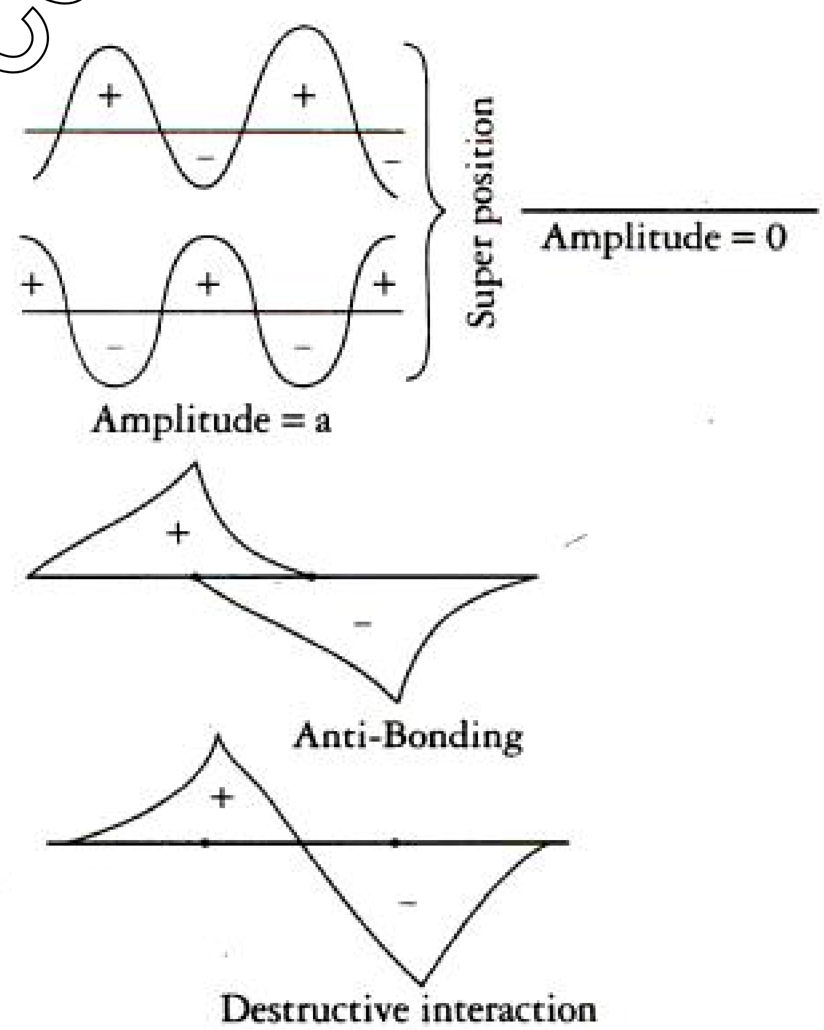
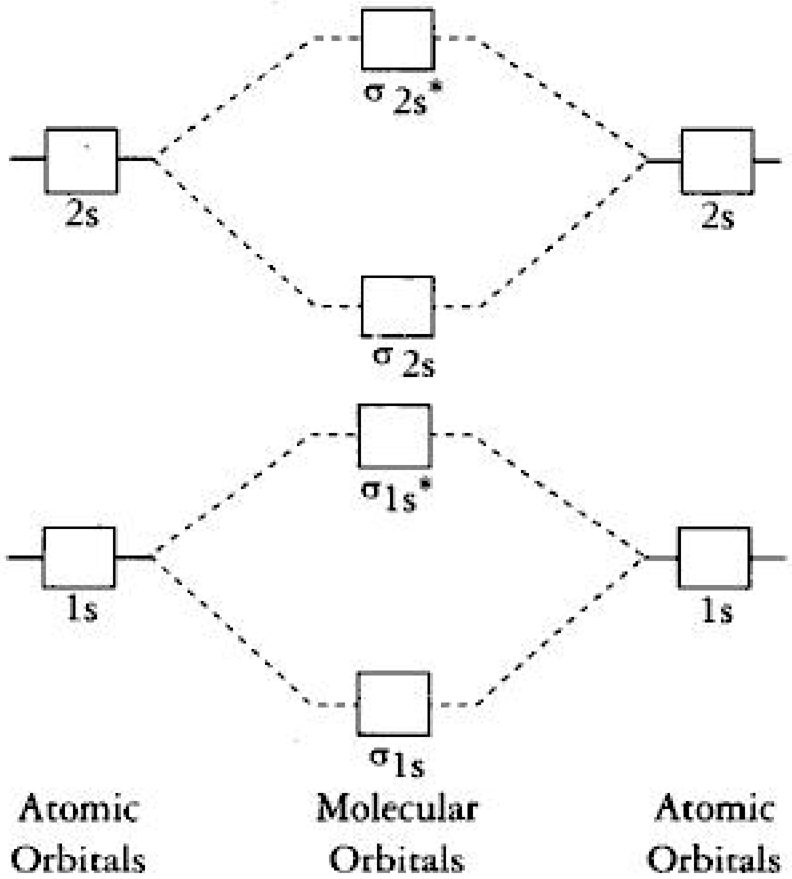


Fig. 1.14

Facts Related to HoMOs and LuMOs

- Energy: LuMOs > HoMOs
- Wavelength: LuMOs < HoMOs



2. Molecular orbital energy level diagram for diatomic homonuclear molecules such as O_2, F_2 etc.
   (i) Molecules with N_2 configuration or 14 e^-.
   $\sigma 1s\ \sigma^* 1s,\ \sigma 2s\ \sigma^* 2s,\ \pi 2p_x \approx \pi 2p_y,\ \sigma 2p_z$
   (ii) Molecules with O_2 configuration or more than 14 e.
   $\sigma 1s\ \sigma^* 1s,\ \sigma 2s\ \sigma^* 2s,\ \sigma 2p_z\ \pi 2p_x \approx \pi 2p_y,\ \pi^* 2p_x \approx \pi^*\ 2p_y,\ \sigma^* 2p_z$

- σ 1s is the lowest energy molecular orbital while $\sigma^* 2p_z$ is the highest energy molecular orbital.
- Due to intermixing of 2s and 2p orbitals in cases where the number of elecruons is more than 16, $\sigma 2p_z$ is taken after $\sigma^* 2s$ here.
- Bond order = $\dfrac{n_b - n_a}{2}$

  Here n_b = Number of bonding molecular orbital electrons

  n_a = Number of anti-bonding molecular orbital electrons

  Bond order ∝ Bond dissociation energy
  ∝ Bond angle
  $\propto \dfrac{1}{\text{Bond length}}$
- Higher the bond order, higher will be stability and shorter will be the bond length.
- If unpaired electrons (n = 1, 2) are present in a molecule it is paramagnetic.
- If n = 0 that is no unpaired electrons, molecule is diamagnetic.

  Examples,

  H_2 : $\sigma(1s)^2$

  H_2^+ : $\sigma(1s)^1$

  H_2^- : $\sigma(1s)^2\ \sigma^*(1s)^1$

  N_2^- : KK $\sigma(2s)^2, \sigma^*(2s)^2, \pi(2px)^2 = \pi(2py)^2, \sigma(2pz)^2\ \pi^*(2px)^1$

  N_2^{2-} : KK $\sigma(2s)^2, \sigma^*(2s)^2, \pi(2px)^2 = \pi(2py)^2, \sigma 2pz^2\ \pi^*(2px)^1 = \pi^*(2py)^1$

  O_2 : KK $\sigma(2s)^2, \sigma^*(2s)^2, \sigma(2pz)^2, \pi(2px)^2 = \pi(2py)^2\ \pi^*(2px)^1 = \pi^*(2py)^1$

  O_2^+ : KK, $\sigma(2s)^2, \sigma^*(2s)^2, \sigma(2pz)^2, \pi(2px)^2\ \pi(2py)^2 = \pi^*(2px)^1$

  O_2^- : KK $\sigma(2s)^2, \sigma^*(2s)^2, \sigma,(2pz)^2, \pi(2px)^2\ \pi(2py)^2, \pi^*(2px)^2 = \pi^*(2py)^1$

  O_2^{2-} : KK, $\sigma(2s)^2\ \sigma^*(2s)^2, \sigma(2pz)^2, \pi(2px)^2 = \pi(2py)^2\ \pi^*(2px)^2 = \pi^*(2py)^2$

  F_2 : KK, $\sigma(2s)^2\ \sigma^*(2s)^2, \sigma(2pz)^2, \pi(2px)^2 = \pi(2py)^2\ \pi^*(2px)^2 = \pi^*(2py)^2$

K K Stands for $\sigma\ 1s^2\ \sigma^*\ 1s^2$ here.

Some Orders Related to Molecular Orbital Theory

	O_2^{2+}	O_2^+	O_2	O_2^-	O_2^{-2}
Bond order	3	2.5	2	1.5	1

  →

  Decreasing order of bond order, bond angle, bond dissociation energy.
  Increasing order of bond length.

- Magnetic Nature

	O_2	>	O_2^-	≈	O_2	>	O_2^{2+}	=	O_2^{2-}
n	2		1		1		0		0
	Paramagnetic		Weakly Paramagnetic						Diamagnetic

- CO, NO^+, CN^-, N_2 (14 e^-) all have bond order 3 and are diamagnetic.
- NO, CN, N_2^-, N_2^+ all have a bond order equal to 2.5 and are paramagnetic as n = 1.
- H_2, Li_2, B_2 all have a bond order equal to one and are diamagnetic except B_2.
- H_2^-, H_2^+, He_2^+ all have a bond equal to order ½ and are paramagnetic.
- All molecules with fractional bond order are paramagnetic.
- Molecules with whole number bond order are mostly diamagnetic, except O_2, B_2, N_2^{2-}.

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34. The number of lone pairs on Xe in XeF_2, XeF_4 and XeF_6, respectively are
(a) 3, 2, 1 (b) 2, 4, 6
(c) 1, 2, 3 (d) 6, 4, 2

35. The two atoms X and Y lie on the top of group 2 and group 16, respectively. On combination, they form compound of the type
(a) X_2Y_2 (b) XY
(c) X_2Y (d) XY_2

36. Pairs of species having identical shapes for molecules is
(a) BF_3, PCl_3 (b) PF_5, IF_5
(c) CF_4, SF_4 (d) XeF_2, CO_2

37. Shape of ClF_3 is
(a) T-shaped (b) V-shaped
(c) Pyramidal (d) Equilateral triangle

38. A square planar complex is formed by hybridization of the following atomic orbitals
(a) s, p_x, p_y, p_z (b) s, p_x, p_y, p_z, d
(c) $dx^2 - y^2$, s, p_x, p_y (d) s, p_x, p_y, p_z, dz^2

39. Which of the following represents the Lewis structure of N_2 molecule?
(a) $\overset{..}{\underset{..}{:N}} \equiv \overset{..}{\underset{..}{N:}}$ (b) $\overset{..}{\underset{..}{:N}} \equiv \overset{..}{\underset{..}{N:}}$
(c) $\overset{..}{\underset{..}{:N}} \equiv \overset{..}{\underset{..}{N:}}$ (d) $\overset{..}{\underset{..}{:N}} - \overset{..}{\underset{..}{N:}}$

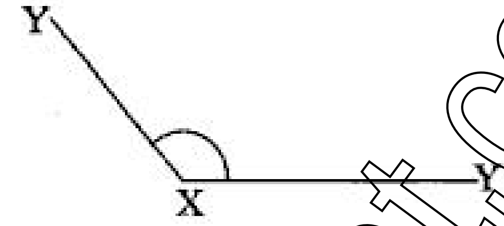
40. Inter-molecular hydrogen bonding exists in
(a) o-nitrophenol
(b) o-chlorophenol
(c) Ammonium chloride
(d) Water

41. The geometrical shape of sp^3d hybridization is
(a) Trigonal bipyramidal
(b) Linear
(c) Tetrahedral
(d) Square planar

42. In which of the following species, intramolecular H-bonding occurs?
I. Acetate ion II. Salicylate ion
III. Propanoic acid IV. O-Nitrophenol
(a) I, III, IV (b) I, II, IV
(c) II, IV (d) IV only

43. Which one of the following compounds has the smallest bond angle in its molecule?
(a) SO_2 (b) OH_2
(c) SH_2 (d) NH_3

44. Which bond angle, θ would result in the maximum dipole moment for the triatomic molecule XY_2 shown below:



(a) $\theta = 120°$ (b) $\theta = 90°$
(c) $\theta = 145°$ (d) $\theta = 175°$

45. Which of the following has the highest bond order?
(a) N_2 (b) O_2
(c) He_2 (d) H_2

46. The energy of hydrogen bond is of the order of
(a) 40 kJ mol^{-1} (b) 140 kJ mol^{-1}
(c) 400 kJ^{-1} (d) 4 kJ mol^{-1}

47. Which one of the following pairs of molecules will have permanent dipole moments for both members?
(a) SiF_4 and NO_2 (b) NO_2 and CO_2
(c) NO_2 and O_3 (d) SiF_4 and CO_2

48. In the formation of N_2^+ from N_2, the electron is removed from a
(a) σ – orbital (b) π – orbital
(c) σ^* – orbital (d) π^* – orbital

49. Which of the following is diamagnetic?
(a) H_2^+ (b) O_2
(c) Li_2 (d) He_2^+

50. How many types of F – S – F bonds are present in SF_4?
(a) 5 (b) 4
(c) 3 (d) 2

51. An octahedral complex is formed when hybrid orbitals of the following type are involved
(a) $d^2 sp^3$ (b) dsp^2
(c) sp^3 (d) sp^2

52. The pair of species having identical shapes for molecules of both species is
(a) CF_4, SF_4 (b) XeF_2, CO_2
(c) BF_3, PCl_3 (d) PF_5, IF_5

53. Among the following compounds, the one that is polar and has the central atom with sp^2 hybridization is

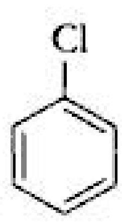
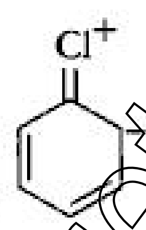
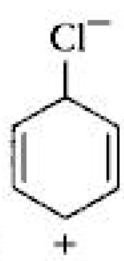
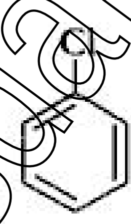
(a) $O_2 < H_2O_2 < O_3$
(b) $O_3 < H_2O_2 < O_2$
(c) $H_2O_2 < O_2 < O_3$
(d) $O_2 < O_3 < H_2O_2$

98. In which one of the following pairs, molecules/ions have similar shape?
(a) CCl_4 and $PtCl_4$
(b) NH_3 and BF_3
(c) BF_3 and t-butyl carbonium ion
(d) CO_2 and H_2O

99. How many bonding MOs can be formulated for benzene and how many of these can degenerate?
(a) 3, 6 (b) 3, 2
(c) 6, 3 (d) 2, 3

100. The correct order of bond angles (smallest first) in H_2S, NH_3, BF_3 and SiH_4 is
(a) $H_2S < SiH_4 < NH_3 < BF_3$
(b) $NH_3 < H_2S < SiH_4 < BF_3$
(c) $H_2S < NH_3 < SiH_4 < BF_3$
(d) $H_2S < NH_3 < BF_3 < SiH_4$

101. Which of the following is not a resonating form of chlorobenzene?

(a) 
(b) 
(c) 
(d) 

102. The bond order in NO is 2.5 while that in NO^+ is 3. Which of the following statements is true for these two species?
(a) bond length in NO^+ is greater than in NO
(b) bond length in NO is greater than in NO^+
(c) bond length in NO^+ is equal than in NO
(d) bond length is unpredictable

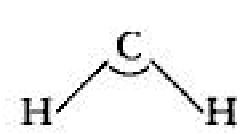
103. The sequence that correctly describes the relative bond strength pertaining to oxygen molecule and its cation or anion is
(a) $O_2^{2-} > O_2^- > O_2 > O_2^+$
(b) $O_2 > O_2^+ > O_2^- > O_2^{2-}$
(c) $O_2^+ > O_2 > O_2^{2-} > O_2^-$
(d) $O_2^+ > O_2 > O_2^- > O_2^{2-}$

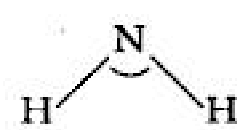
104. The dipole moments of methane and its halogen derivatives are in the order
(a) $CH_4 < CH_2Cl_2 < CHCl_3 < CH_3Cl$
(b) $CH_3Cl < CH_2Cl_2 < CHCl_3 < CH_4$
(c) $CH_4 < CHCl_3 < CH_2Cl_2 < CH_3Cl$
(d) $CH_4 < CH_3Cl < CH_2Cl_2 > CHCl_3$

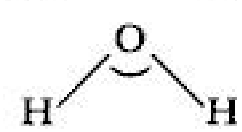
105. The correct order of increasing bond angles is
(a) $OF_2 < H_2O < Cl_2O < ClO_2$
(b) $ClO_2 < OF_2 < Cl_2O < H_2O$
(c) $ClO_2 < Cl_2O < H_2O < OF_2$
(d) $OF_2 < Cl_2O < H_2O < ClO_2$

106. The correct order of bond energies for the C-H bond is
(a) $(CH_3)_3C\text{-}H < (CH_3)_2CH\text{-}H < H_3C\text{-}H < H_3C.CH_2\text{-}H$
(b) $H_3C\text{-}H < (CH_3)_3C\text{-}H < H_3C.CH_2\text{-}H < (CH_3)_2CH\text{-}H$
(c) $(CH_3)_3C\text{-}H < (CH_3)_2CH\text{-}H < H_3C.CH_2\text{-}H < H_3C\text{-}H$
(d) $H_3C\text{-}H < H_3C.CH_2\text{-}H < (CH_3)_2CH\text{-}H < (CH_3)_3C\text{-}H$

107. The bond lengths and bond angles in the molecules of methane, ammonia and water are given as under:


0.109nm; 109.5°


0.101nm; 107°


0.096nm; 104.5°

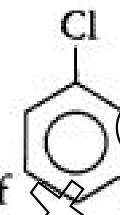
The variation in bond angle is a result of
I. The increasing repulsion between hydrogen atoms as the bond length decreases.
II. The number of non-bonding electron pairs in the molecule.
III. A non-bonding electron pair having a greater repulsive force than a bonding electron pair.

140. The number of sigma and pi-bonds in the compound $(CN)_2C = C(CH_3)(MCO)_3$ is
(a) 16 σ and 10 π bonds
(b) 15 σ and 11 π bonds
(c) 17 σ and 11 π bonds
(d) 16 σ and 11 π bonds

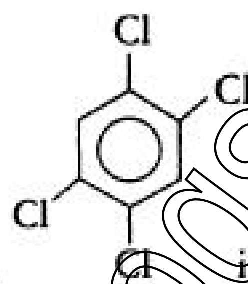
141. Consider the given statements about the molecule: $(H_3C)_2\,CH - CH = CH - C \equiv C - CH = CH_2$.
I. Three carbon atoms are sp^3 hybridized
II. Three carbon atoms are sp^2 hybridized
III. Two carbon atoms are sp hybridized of three statements:
(a) I and II are correct
(b) I and III are correct
(c) II and III are correct
(d) I, II and III are correct

142. The correct decreasing order of bond angles is
(a) $ClF_3 > PF_3 > NF_3 > BF_3$
(b) $BF_3 > PF_3 > NF_3 > ClF_3$
(c) $BF_3 > NF_3 > PF_3 > ClF_3$
(d) $BF_3 > ClF_3 > PF_3 > NF_3$

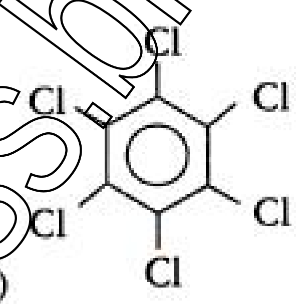
143. The correct order of bond energies for the C-H bond is
(a) $(CH_3)_3C\text{-}H < (CH_3)_2CH\text{-}H < H_3C\text{-}H < H_3C.CH_2\text{-}H$
(b) $H_3C\text{-}H < (CH_3)_3C\text{-}H < H_3C.CH_2\text{-}H < (CH_3)_2CH\text{-}H$
(c) $(CH_3)_3C\text{-}H < (CH_3)_2CH\text{-}H < H_3C.CH_2\text{-}H < H_3C\text{-}H$
(d) $H_3C\text{-}H < H_3C.CH_2\text{-}H < (CH_3)_2CH\text{-}H < (CH_3)_3C\text{-}H$

144. The dipole moment of 

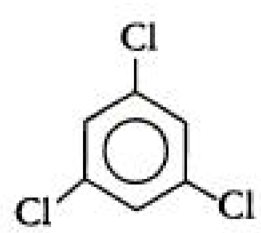
is X. The dipole moment of:

(a) 

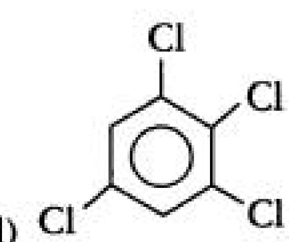
is $4X\sqrt{3}$

(b) 

is 3X

(c) 

is $6X\sqrt{2}$

(d) 

X.

Multiple Correct Answer Type Questions (More Than One Choice)

145. Which of the following statement(s) is/are correct?
(a) The crystal lattice of ice is mostly formed by the covalent as well as hydrogen bonds.
(b) The density of water increases when heated from 0°C to 4°C due to the change in the structure of the cluster of water molecules.
(c) The density of water increases from 0°C to a maximum at 4°C because the entropy of the system increases.
(d) Above 4°C the thermal agitation of water molecules increases. Therefore, intermolecular distance increases and water starts expanding.

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Comprehension–2

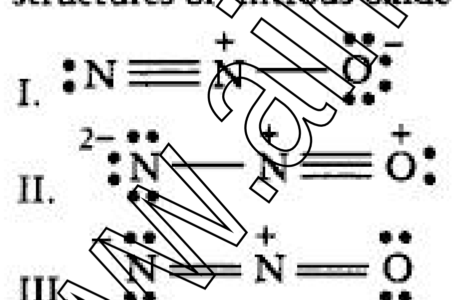
A number of molecules and polyatomic ions cannot be described accurately by a single Lewis structure and a number of descriptions based on the same skeletal structure are written and these taken together represent the molecule or ion. These structures have almost similar energies, same arrangement of atoms and have same number of bonding and non-bonding pair of electrons. These contributing structures or canonical forms taken together constitute the resonance hybrid which represents the molecule or ion.

185. Which of the following is not correct about resonance?
   (a) It averages the bond features as a whole.
   (b) It stabilizes the molecule since energy of the resonance hybrid is lower than that of any of the single canonical structure.
   (c) There is no equilibrium between these canonical structures.
   (d) These canonical structures have real existence also.

186. The value of bond order of CO bond for CO_3^{2-} ion is
   (a) 1.25 (b) 1.33
   (c) 1.5 (d) 1.0

187. Due to resonance in benzene, the value of C-C bond length and bond order are, respectively
   (a) 115 pm and 1.5
   (b) 1.39 Å and 1.33
   (c) 1.39 Å and 1.5
   (d) 115 pm and 2.0

188. The correct order of stability for the resonating structures of nitrous oxide can be given as



   (a) III > II > I (b) I > II > III
   (c) I > III > II (d) I > II = III

Comprehension–3

Pauling introduced the concept of hybridization of atomic orbitals for explaining the characteristic shapes of polyatomic molecules. For example sp, sp^2 and sp^3 hybridizations of atomic orbitals of Be, B, C, N, P and O are used to explain the formation and geometrical shapes of molecules like $BeCl_2$, BF_3, CCl_4, PH_3 and H_2O. They also explain the formation of multiple bonds in molecules like ethyne and ethene.

189. Which is not correct regarding hybridization?
   I Hybrid orbitals are formed when atomic orbitals have comparable energies.
   II. For hybridization atomic orbitals must be fairly apart.
   III. Hybrids always have identical energy and identical shapes.
   IV. The electron waves in hybrid orbitals attract each other.
   (a) I and II (b) II and III
   (c) III and IV (d) I and III

190. Which of there is correctly matched?

Molecule	Hybridization of central atom
I. IF_4^+	sp^3d
II. ICl_4^-	sp^3d^2
III $BeCl_2$ in solid state	sp^2
(IV) PCl_4^+	dsp^2

   (a) I and II (b) I and III
   (c) II and III (d) I, II and IV

191. In hepta-3-ene and 1-yne, the hybridization state of carbon atom number 2 and 3 are, respectively
   (a) sp^2 and sp, respectively
   (b) sp and sp^2 respectively
   (c) sp only
   (d) sp and sp^3 respectively

192. In which of the following change, the hybridization state of central atom does not change?
   (a) Conversion of $AlCl_3$ into Al_2Cl_6
   (b) PCl_5 into PCl_6^-
   (c) Toluene into benzaldehyde
   (d) NH_3 into NCl_3

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Comprehension–2

185. (d) 186. (b) 187. (c) 188. (c)

Comprehension–3

189. (c) 190. (a) 191. (b) 192. (d)

Comprehension–4

193. (b) 194. (b) 195. (c) 196. (d)

Comprehension–5

197. (d) 198. (b) 199. (c) 200. (c)

Assertion and Reasoning Questions

201. (b) 202. (a) 203. (b) 204. (c)
205. (a) 206. (b) 207. (b) 208. (a)
209. (c) 210. (c) 211. (a) 212. (a)
213. (c) 214. (d) 215. (b) 216. (a)
217. (b) 218. (c) 219. (a) 220. (a)
221. (a) 222. (b) 223. (a) 224. (d)
225. (a)

Matrix–Match Type Questions

226. (a)-(q), (b)-(p, t), (c)-(r, t), (d)-(s)
227. (a)-(s), (b)-(r), (c)-(q), (d)-(p)
228. (a)-(r, t), (b)-(p), (c)-(q, t), (d)-(s)
229. (a)-(r, t), (b)-(q), (c)-(s), (d)-(p, t)
230. (a)-(p), (b)-(p, q), (c)-(p, q, r, s), (d)-(p, q, s)
231. (a)-(p), (b)-(t), (c)-(s), (d)-(r)
232. (a)-(s), (b)-(q, t), (c)-(p), (d)-(r, t)
233. (a)-(p, s), (b)-(q), (c)-(r, s), (d)-(t)
234. (a)-(q), (b)-(p), (c)-(s), (d)-(r)
235. (a)-(r), (b)-(s, t), (c)-(p), (d)-(q)
236. (a)-(r, t), (b)-(p, t), (c)-(q), (d)-(s)
237. (a)-(r), (b)-(s), (c)-(p), (d)-(p)
238. (a)-(s), (b)-(p), (c)-(q), (d)-(r)
239. (a)-(p), (b)-(r), (c)-(q), (d)-(s)
240. (a)-(r), (b)-(s), (c)-(p), (d)-(q)

The IIT–JEE Corner

241. (c) 242. (b) 243. (c) 244. (a)
245. (b) 246. (d) 247. (b) 248. (a)
249. (a) 250. (b) 251. (a) 252. (a)
253. (a) 254. (b) 255. (d) 256. (b)
257. (b) 258. (d) 259. (d) 260. (d)
261. (b) 262. (d) 263. (a)

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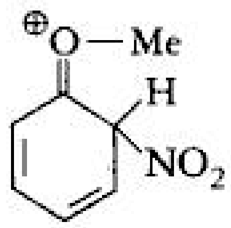
123.  Since in this structure, every atom (except H) has a stable octet of electrons, hence it is the most stable one.

124. In XeF_4: sp^3d^2 hybridization. Shape is square planar instead of octahedral due to presence of two lone pair of electrons on Xe atom.

SF_4: SF_4 molecules shows sp^3d.

125. A compound is soluble in water when its hydration enthalpy is greater than its lattice enthalpy.

128. $CuSO_4 \cdot 5H_2O$

$$Cu^{++} + O{=}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{S}}{-}O^- \;.\, 5H_2O$$

Here, ionic and covalent bonds are present in $CuSO_4$ while H_2O molecules are attached by coordinate bonds.

132. Here the order of dipole moment will be

(A) > (B) > (C) = (D).

134. Moles of (P) = $\frac{254}{127} = 2$

Moles of (Q) = $\frac{80}{16} = 5$

Hence, the formula is P_2Q_5.

135. As N_2 has no unpaired electron while NCl (isoelectronic with O_2 in terms of valence electrons) has two unpaired electrons.

138. By Pauling's rule, the ionic radius is inversely proportional to the effective nuclear charge. Thus,

$$r_{K^+} = \frac{\text{cosnt (c)}}{19 - 10.87} = \frac{c}{8.13};$$

$$r_{Cl^-} = \frac{c}{17 - 10.87} = \frac{c}{6.13};$$

$$r_{K^+} + r_{Cl^-} = c(1/8.13 + 1/6.13) = 3.14 Å$$

$$r_{K^+} / (r_{K^+} + r_{Cl^-}) = \frac{6.13}{6.13 \times 8.13}.$$

$$r_{K+} = \frac{6.13}{14.26} \times 3.14 = 1.35 Å$$

141. This molecule has four carbon atoms (i.e., $-CH = CH-$ and $-CH = CH_2$) sp^2 hybridized.

142. As for them the bond angles are BF_3 – 120°, NF_3 – 106°, PF_3 – 101°, ClF_3 – 90° and 180°.

Multiple Correct Answers Type Questions

148. As XeF_2 has three lone pair of electrons hence it is incorrect.

157. As boiling point of HF is +19.5°C, boiling point of CH_3F = –78°C.

159. As the bond order of these species are

CN = 2.5

N_2 = 3.0

CO = 3.0

CN^- = 3.0

NO^+ = 3.0

163. As in SF_6 there are 12 electrons in the valence shell of sulphur atom hence it is correct.

166. The bond angle of PF_3 is more than PCl_3 because of pπ-dπ bonding in PF_3

As bond order of NO^{2+} and NO is same i.e., 2.5 so the correct order is

$NO^+ > NO^{2+} = NO > NO^-$.

169.

SiF_4	sp^3	tetrahedral	non-polar
XeF_4	sp^3d^2	square planar	non-polar
SF_4	sp^3d	square pyramidal	polar
BF_3	sp^2	trigonal planar	non-polar

171. $NaHCO_3 \longrightarrow Na^+ + HCO_3^-$

Ionic bond

$$H{-}O{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O^{\ominus}$$

Covalent bond

180. $SnCl_2$ has sp^2 hybridization and angular structure. In CS_2 carbon is sp hybridized and is linear. NCO^- and NO_2^+ being isoelectronic with CS_2 have same type of shape.

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Solution

If there were opposite charges of one fundamental unit, i.e.,

q= = 1.602×10^{-19} coulombs, then

$\mu = q \times d$

$= (1.602 \times 10^{-19}$ coulombs$) \times (2.6 \times 10^{-10}$m)

$= 4.1652 \times 10^{-29}$ coulombs metre

As $\mu_{observed} = 3.336 \times 10^{-29}$ coulomb metre

Hence % ionic character $\mu_{observed}$

$= 3.336 \times 10^{-29} \times 100$

4.1652×10^{-29}

= 80.09 %

15. Find the dipole moment of HCl molecule if the bond length is 1.2475 (if D = 3.336×10^{-30} CM).

Solution

$\mu = q.r = (1.6023 \times 10^{-19}\ C)(1.2476 \times 10^{-10} m)$

$= 1.999 \times 10^{-29}$ C-m

$$\mu = \frac{1.999 \times 10^{-29}\ C\text{-}m}{3.336 \times 10^{-30}\ C\text{-}m\ D^{-1}}$$

= 5.99D

16. Explain the difference in the nature of bonding in LiF and LiI.

[*IIT 1996*]

Questions For Self-Assessment

17. Using the VSEPR theory, identify the type of hybridization and draw the structure of OF_2. What are the oxidation states of O and F?
[*IIT 1996*]

18. Interpret the nonlinear shape of H_2S molecule and nonplanar shape of PCl_3 using valence shell electron pair repulsion (VSEPR) theory. (Atomic number H = 1, P = 15, Cl = 17)
[*IIT 1998*]

19. Write the MO electron distribution of O_2. Specify its bond order and magnetic property.
[*IIT 2000*]

20. Using VSEPR theory, draw the shape of PCl_5 and BrF_5.
[*IIT 2003*]

21. Which one is more stable in diethyl ether, anhydrous $AlCl_3$ or hydrous $AlCl_3$? Explain in terms of bonding.
[*IIT 2003*]

22. Draw the shape of XeF_4 and OSF_4 according to VSEPR theory. Show the lone pair of electrons on the central atom.
[*IIT 2003*]

23. On the basis of ground state electronic configuration arrange the following molecules in increasing O – O bond length order.

KO_2, O_2, $O_2[AsF_6]$

[*IIT 2003*]

24. Predict whether the following molecules are isostructural or not. Justify your answer.

(i) NMe_3

(ii) $N(SiMe_3)_3$

[*IIT 2005*]

25. What is the effect of the following ionization processes on the bond orders in C_2 and O_2?

26. How does bond energy vary from N^-_2 to N^+_2 and why?

27. What is the hybrid state of $BeCl_2$? What will be the change in the hybrid state of $BeCl_2$ in the solid state?

28. BeF_2 and BF_3 both are stable inspite of contraction of octet rule. Why?

29. PX_5 exists but not PH_5. Explain?

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Factors Affecting Electronegativity

(i) Electronegativity $\propto$ Zeff
$\propto$ 1/Size

(ii) Ionization Energy and Electron Affinity:
Electronegativity $\propto$ Ionization energy
$\propto$ Electron affinity

(iii) **Charge on Atom:** The cation will be more electronegative than parent atom, which in turn will be more electronegative than its anion. Higher the positive charge (oxidation state) greater will be its electronegativity.

For example, $Fe^{+3} > Fe^{+2}$

(iv) **Effect of Substitution:** The electronegativity of an atom depends upon the nature of substituent attached to that atom.

For example, carbon atom in CF_3I acquires greater positive charge than in CH_3I, therefore C atom in CF_3I is more electronegative than in CH_3I.

(v) The difference in electronegativity of an atom caused by substituents results in different chemical behaviour of that atom.

(vi) Electronegativity $\propto$ s percentage

So, $sp > sp^2 > sp^3$

For example,

$C \equiv C^- > C = C^- > C - C^-$
↓
more electronegative

Variation in Electronegativity Value

In Period

On moving from left to right in a period the electronegativity increases as Zeff increases and size decreases.

Order for first electronegativity in any Period

IA < IIA > IIIA < IVA < VA > VIA < VIIA
Min. Max.

For example,

Li < Be < B < C < N < O < F
Na < Mg < Al < Si < P < S < Cl

In any period halogens have maximum value of electronegativity while alkali metals have lowest of electronegativity.

Electronegativity of zero group elements is zero. Since, they have stable octet state they have no tendency to attract electrons.

In Group:

On moving from top to bottom in a group electronegativity decreases as Zeff decreases and size increases.

For example,
F > Cl > Br > I
O > S > Se > Te
N > P > As > Sb

Group →	1 IA	2 IIA	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA
I Period	H 2.1						
II Period	Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
III Period	Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
IV Period	K 0.8	Ca 1.0	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
V Period	Rb 0.8	Sr 1.0	In 1.7	Sn 1.8	Sb 1.9	Te 2.01	I 2.5
VI Period	Cs 0.7	Ba 0.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 1.76	At 2.2

Decreases ↓ (down a group); Increases → (across a period)

REMEMBER

Decreasing order of electronegativity

- F > O > N > Cl > C > B
- 4 3.5 3 2.97 2.5 2
- Almost all metalloids have nearly 2 value of electronegativity.

Applications of Electronegativity

(1) **Calculation of partial ionic character in a covalent bond:** It depends upon two factors:

(i) The electronegativity difference between two bonded atoms.

(ii) Dipole moment of the compound.
Hannay and Smyth Equation:

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14. Four successive members of the first row transition elements are listed with their atomic numbers. Which one of them is expected to have the highest third ionization energy?
(a) iron (Z = 26)
(b) vanadium (Z = 23)
(c) manganese (Z = 25)
(d) chromium (Z = 24)

15. Identify the correct order in which the covalent radius of the following elements increases
(I) Ti (II) Ca
(III) Sc
(a) (I) (II) (III) (b) (II) (I) (III)
(c) (I) (III) (II) (d) (III) (II) (I)

16. Which one of the following arrangements represents the correct order of electron gain enthalpy (with negative sign) of the given atomic species?
(a) S < O < Cl < F (b) Cl < F < S < O
(c) F < Cl < O < S (d) O < S < F < Cl

17. The electronic affinity values (in kJ mol^{-1}) of three halogens X, Y and Z are, respectively −349, −333 and −325. Then X, Y and Z respectively are
(a) F_2, Cl_2 and Br_2 (b) Cl_2, F_2 and Br_2
(c) Cl_2, Br_2 and F_2 (d) Br_2, Cl_2 and F_2

18. Which one of the following orders is not in accordance with the property stated against it?
(a) $F_2 > Cl_2 > Br_2 > I_2$; electronegativity
(b) $F_2 > Cl_2 > Br_2 > I_2$; bond dissociation energy
(c) $F_2 > Cl_2 > Br_2 > I_2$; oxidizing power
(d) HI > HBr > HCl > HF; acidic property in water

19. A sudden large jump between the values of second and third ionization energies of elements would be associated with which of the following electronic configuration?
(a) $1s^2\ 2s^2\ 2p^6\ 3s^1$
(b) $1s^2\ 2s^2\ 2p^6\ 3s^2$
(c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$
(d) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

20. Atomic radii of fluorine and neon in Angstrom units are, respectively given by
(a) 1.60, 1.60 (b) 0.72, 0.72
(c) 0.72, 1.60 (d) 1.60, 0.72

21. Amongst the following elements (whose electronic configurations are given), the correct increasing order of ionization energy is
(I) [Ne] $3s^2\ 3p^1$ (II) [Ne] $3s^2\ 3p^3$
(III) [Ne] $3s^2\ 3p^2$ (IV) [Ar] $3d^{10}\ 4s^2\ 4p^3$
(a) III < I < II < IV (b) IV < II < III < I
(c) I < III < IV < II (d) II < IV < I < III

22. The statement that is not correct for periodic classification of elements is
(a) The properties of elements are a periodic function of their atomic numbers.
(b) Nonmetallic elements are less in number than metallic elements.
(c) The first ionization energies of elements along a period do not vary in a regular manner with increase in atomic number.
(d) For transition elements, the d-subshells are filled with electrons monotonically with increase in atomic number.

23. Sodium forms Na^+ ion but it does not form Na^{2+} because
(a) very low value of $(IE)_1$ and $(IE)_2$.
(b) very high value of $(IE)_1$ and $(IE)_2$.
(c) low value of $(IE)_1$ and low value of $(IE)_2$.
(d) low value of $(IE)_1$ and high value of $(IE)_2$.

24. Correct order of (IE) among the elements Be, B, C, N, O is
(a) B < Be < C < O < N
(b) B < Be < C < N < O
(c) Be < B < C < N < O
(d) Be < B < O < N < C

25. Which of the following order is wrong?
(a) $NH_3 < PH_3 < AsH_3$ — acidic
(b) Li < Be < B < C — $(IE)_1$
(c) $Al_2O_3 > MgO < Na_2O < K_2O$ — Basic
(d) $Li^+ < Na^+ < K^+ < Cs^+$ — ionic radius

26. Amongst the following elements (whose electronic configurations are given), the one having the highest ionization energy is
(a) [Ne] $3s^2\ 3p^1$ (b) [Ne] $3s^2\ 3p^3$
(c) [Ne] $3s^2\ 3p^2$ (d) [Ar] $3d^{10}\ 4s^2\ 4p^3$

27. The outermost electronic configuration of the most electronegative element is
(a) $ns^2\ np^3$ (b) $ns^2\ np^4$
(c) $ns^2\ np^5$ (d) $ns^2\ np^6$

Multiple Correct Answer Type Questions (One or More Than One Choice)

66. Choose the correct statement.
(a) Ce, Gd, U are lanthanoid.
(b) Cu, Ag, Au are known as coinage metal.
(c) Li although the first member of alkali metal but it is strongest reducing agent.
(d) Reducing character decreases down the group.

67. Which of the following represent the incorrect order of ionization energies?
(a) F > N > O > C (b) F > O > N > C
(c) I > Br > F > Cl (d) F > Cl > Br > I

68. Choose the correct statement/s.
(a) $1s^2$ element belongs to p-block.
(b) [Xe] $4f^{14}$ $5d^1$ $6s^2$ element belong to f-block.
(c) [Ar] $3d^5$ $4s^1$ element belong to s-block.
(d) [Ar] $3d^{10}$ $4s^2$ $4d^6$ element is noble gas.

69. Choose the correct order.
(a) $Be^{2+} < Li^+ < Ca^{2+} < K^+$ (ionic radii).
(b) Sulphur has highest electron affinity among chalcogens.
(c) Cl has highest negative electron gain enthalpy.
(d) F is second most electronegative element.

70. Which of the following is/are correct order regarding radius?
(a) $Al^{3+} < Mg^{2+} < Na^+$
(b) $B^{3+} < Ga^{3+} < Al^{3+}$
(c) $Be^{2+} < B^{3+} < Li^+$
(d) $Cl^- < S^{2-} < P^{3-}$

71. Which of the following element are artificially made and do not exist in nature?
(a) Bi (b) Ge
(c) Tc (d) At

72. Which of the following pairs contain metalloid?
(a) In, Tl (b) Ge, Ga
(c) As, Te (d) I, Bi

73. Which of the following statement is/are correct?
(a) Fluorine has the highest electron affinity.
(b) Helium has the highest ionization energy.
(c) Alkali metals are the strongest oxidizing agents.
(d) Carbon has the highest melting point.

74. Choose the pair in which IE_1 of first element is greater than IE_1 of second element but in case of IE_2 order is reversed.
(a) P, S (b) F, O
(c) Mg, Al (d) N, O

75. Which of the following pair of oxides are neutral?
(a) Al_2O_3 and B_2O_3
(b) MnO and Mn_2O_7
(c) CO and H_2O
(d) NO and N_2O

76. In halogens, which of the following property increases from iodine to fluorine?
(a) Electronegativity
(b) Bond length
(c) Reducing power
(d) Ionization energy of the element

77. Select the process which is/are endothermic here.
(a) $H + e^- \longrightarrow H^-$
(b) $O^- + e^- \longrightarrow O^{2-}$
(c) $Ar - e^- \longrightarrow Ar^+$
(d) $X \longrightarrow X^+ + e^-$

78. Which of the following sets of ions are isoelectronic?
(a) Li^+, Be^{2+}, Be^{3+} (b) Na^+, Mg^{2+}, Al^{3+}
(c) P^{3-}, S^{2-}, K^+ (d) Cl^-, Br^-, I^+

79. Which of the following sequence contains atomic number of only representative elements?
(a) 13, 33, 54, 83 (b) 55, 12, 48, 53
(c) 22, 33, 55, 66 (d) 3, 33, 53, 87

80. Which of the following pairs has elements that belong to the same period?
(a) Ca and Zn (b) Mg and As
(c) Ca and Ar (d) Na and Cl

81. Choose the correct order:
(a) Reducing strength of the element depends on the magnitude of the ionization energy.
(b) Mo (IV) > Mo (III) > Mo (II) (Electronegativity order)

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111. (A): Ionization energy of magnesium is more than that of aluminium.
(R): In aluminium 3p-orbital is completely filled whereas in magnesium it is not completely filled.

112. (A): Fluorine is more electronegative than chlorine.
(R): Fluorine is smaller in size than chlorine.

113. (A): Ionization energy for s-electrons is more than the p-electrons for the same shell.
(R): s-electrons are closer to the nucleus than p-electrons hence more tightly attached.

114. (A): Li and Mg show diagonal relationship.
(R): Li and Mg have same atomic radius.

115. (A): He and Be both have the same outer electronic configuration like ns^2 type.
(R): Both are chemically inert.

116. (A): The first ionization energy of N is more stable than that of O.
(R): Oxygen after losing one electron gets a stable electronic configuration.

117. (A): For noble gases in the solid state the crystal radii are actually van der Waal's radii.
(R): In crystals of noble gases no chemical forces operate between the atom.

118. (A): Electron gain enthalpy of oxygen is less than that of fluorine but greater than that of nitrogen.
(R): Ionization enthalpy is as follows
N > O > F

119. (A): Second ionization enthalpy will be higher than the first ionization enthalpy.
(R): Ionization enthalpy is a quantitative measure of the tendency of an element to lose electron.

120. (A): Noble gases have large positive electron gain enthalpy.
(R): Electron has to enter the next higher principle quantum level.

Matrix–Match Type Questions

	p	q	r	s	t
(A)	O	O	O	O	O
(B)	O	O	O	O	O
(C)	O	O	O	O	O
(D)	O	O	O	O	O

121. Match the following:

Column I	Column II
A. F	(p) Smallest anion
B. Cl	(q) Most electronegative
C. Br	(r) Maximum electron affinity
D. I	(s) Metallic lusture
	(t) Pungent liquid

122. Match the following:

Column I	Column II
A. Nonmetal	(p) Halogens
B. High ionization energy	(q) Inert gases
C. Low boiling point	(r) Alkali metals
D. Maximum electron affinity	(s) Transition metals

123. Match the following:

Column I	Column II
A. Nitrogen	(p) Metal
B. Oxygen	(q) Electropositive
C. Calcium	(r) Electronegative
D. Cesium	(s) High ionization energies

124. Match the following:

Column I	Column II
A. F_2	(p) Gaseous molecules
B. O_2	(q) Highest bond energy
C. N_2	(r) Paramagnetic nature
D. Cl_2	(s) Diamagnetic

125. Match the following:

Column I	Column II
A. Reductants	(p) Calcium
B. Strongest oxidant	(q) Sulphur
C. Basic oxides	(r) Fluorine
D. Acidic oxides	(s) Cesium

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46. Chlorine being the group 17 element has maximum electronegativity. 'N' has zero electron affinity because extra stability is associated with exactly half-filled orbitals. Sulphur has more electron affinity than 'O' because the effect of small size of O atom is more than offset by the repulsion of electrons already present in 2p-orbitlas of O atom.

49. As ionization energy decreases with the increase in number of orbits or down the group.

50. As the difference between I_3 and I_4 is maximum so the element (P) has three valence electrons as after losing three electrons it acquires noble gas configuration.

51. Since fluorine atom has a smaller size than iodine, it has greater electron attracting power and so it is a better oxidizing agent.

53. Cr : [Ar] [↑|↑|↑|↑|↑] [↑]
$3d^5$ $4s^1$

Cr^+: [Ar] [↑|↑|↑|↑|↑] [ ]
$3d^5$ $4s^0$

(by first I.P.)
This is stable electronic configuration hence formation of Cr^{2+} by second IP requires maximum enthalpy.

55. Here, X is Mg, Y is Al, Z is Si as MgO is ionic, Al_2O_3 is amphoteric and SiO_2 is a giant molecule.

56. Molar volume $= \dfrac{26.98 \text{ cm}^3}{2.70}$

$= \dfrac{4}{3}\pi r^3 \times 6.02 \times 10^{23}$

$r^3 = \dfrac{26.98}{2.70} \times \dfrac{10^{24} \times 3}{4 \times 3.14 \times 6.02 \times 10^{23}} (\text{Å})^3$

$= \dfrac{10^2 \times 3}{4 \times 3.14 \times 6.02}$

$r = (300 / 12.56 \times 6.02)^{1/3}$

$= 1.583$ Å

59. The first ionization energy values of Na, Mg and Al are 5.1, 7.6 and 6.0 eV. The second ionization energy values of Na, Mg and Al are 47.3, 15.03 and 18.82 eV.

60. $Cl + e^- \longrightarrow Cl^- + 3.7$ eV
35.5 $\quad$ 3.7 × 23.06 kcal

As energy released for conversion of 4 g gaseous chlorine into Cl^- ions

$= \dfrac{3.7 \times 23.06}{35.5} \times 4 = 9.6$ kcal

61. The difference in atomic radii is maximum in Na and K.

62. The fifth ionization energy shows a sudden increase (most likely 1s-orbital)
The likely electron configuration is $1s^2\, 2s^2\, 2p^2$.

63. Element X can lose its first two outermost electrons easily. It is most likely bivalent. By similar reasoning element Y is tetravalent. Therefore, the compound may be X_2Y.

64. $E_1 : E_2 = 0.475 : 1.$
Using the proportionally constant k,
$E_1k + E_2k = 2226$ kJ/mol.
While $E_1k / E_2k = 0.475/1.$
On solving,
$E_2k = 2226 \times 1/1.475 = 1509$ kJ/mol.

65. Half-filled $2p^3$ subshell of O^+ is more stable than $2p^4$ subshell of F^+ So IE_2 of O will be greater than that of F^+.

Multiple Correct Answer Type Questions

96. IE_2 of Na is greater than Mg because second electron is to be removed from stable noble gas configuration in case of sodium.

Comprehension–3

105. As (a) is boron and (b) is aluminium and both these elements are present in IIIA group.

106. As atomic radii is directly proportional to number of orbits and inner shell electrons while inversely proportional to number of valence electrons. Hence, the correct order of size is

E > B > C > D > A

107. E < B < C < A < D
or

Ca	Al	P	B	Cl
–	–50	–74	–83	–349 kJ mol^{-1}

108. B < E < A < C < D
or

Al	Ca	B	P	Cl
577	590	801	1011	1255 kJ mol^{-1}

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PREPARATION AND PROPERTIES OF NONMETALS

3

Chapter Contents

Isolation/preparation and properties of boron, silicon, nitrogen, phosphorous, oxygen, sulphur and halogens, properties of allotropes of carbon (diamond and graphite), phosphorous and sulphur and various levels of multiple-choice questions.

BORON

Occurrence

Boron is not present in free state in nature. In the combined state, it is present in the form of the salts of boric acid. Some of the important minerals of boron are as follows:

1. Borox — $Na_2B_4O_7.10H_2O$
2. Colemanite — $Ca_2B_6H_{11}.5H_2O$
3. Kernite (Rasorite) — $Na_2B_4O_7.4H_2O$
4. Boracite — $2Mg_3B_8O_{15}.MgCl_2$
5. Boric acid — H_3BO_3
6. Boronatrocalcite — $CaB_4O_7.NaBO_2.8H_2O$

Extraction of Boron

1. From Borax or Colemanite
   Boron can be extracted from borax or colemanite ores in two steps:

(i) *Preparation of B_2O_3:*

(a) **From Borax:** First of all, finely powdered borax is converted into B_2O_3 by heating it with conc. HCl or H_2SO_4 as follows:

$$Na_2B_4O_7 + 2HCl \longrightarrow 2NaCl + \underset{\text{Tetraboric acid}}{H_2B_4O_7}$$

$$Na_2B_4O_7 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2B_4O_7$$

$$H_2B_4O_7 + 5H_2O \longrightarrow \underset{\text{Ortho boric acid}}{4H_3BO_3}$$

$$2H_3BO_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O$$

or

$$Na_2[B_4O_5(OH)_4].8H_2O \xrightarrow{\text{acid}} \underset{\text{Orthoboric acid}}{H_3BO_3} \xrightarrow{\text{heat}} B_2O_3$$

(b) **From Colemanite:** The powdered form of colemanite is fused with sodium carbonate and the fused mass is treated with hot water in which calcium carbonate is insoluble and hence gets precipitated. The filtrate solution having borax and

11. Formation of Binary Compounds with Metals

Both can react with many metals forming binary compounds called borides and silicides respectively. For example,

$$2B + 3Mg \xrightarrow{\Delta} \underset{\text{Magnesium boride}}{Mg_3B_2}$$

$$Si + 2Mg \xrightarrow[\text{(In absence of air)}]{\Delta} \underset{\text{Magnesium silicide}}{Mg_2Si}$$

Some of these borides and silicides on hydrolysis results boranes and silanes, respectively.

SILICON

Silicon is the second most abundant element (28 percent by weight) in earth crust. It is widely present as silica (SiO_2).

Three crystalline modifications of SiO_2 are quartz, cristobalite and tridymite of which first two are important. Quartz is used as a piezoelectric material.

Silica occurs as silicates mainly because silica has a great affinity for oxygen. For example, aluminium silicate {Rock clay} (most widely distributed).

Preparation

1. From Silica

   Here silica is reduced by coke in an electric furnace to get silicon.

   $$SiO_2 + 2C \longrightarrow Si + 2CO$$

   $$Si + C \longrightarrow SiC$$

   $$2SiC + SiO_2 \longrightarrow \underset{\text{Crystalline form}}{3Si} + 2CO$$

2. Silica can also be reduced into silicon by magnesium powder.

   $$SiO_2 + 3Mg \longrightarrow \underset{\text{Amorphous form}}{Si} + 2MgO$$

3. From Silicon Tetrachloride

   Ultra pure silicon is obtained by zone refining and by the reduction of very pure $SiCl_4$.

   $$SiCl_4 + 2H_2 \longrightarrow Si + 4HCl$$

4. From Silicon Hydride

   $$SiH_4 \xrightarrow{402^\circ C} Si + 2H_2$$

   It is purified by zone refining process.

Physiochemical Properties

1. It is a very hard solid element which has two allotropic forms i.e.,

(a) **Amorphous:** It is dark brown powder and a more reactive form.

(b) **Crystalline:** It is yellow crystalline solid, iso structural to diamond and less reactive.

2. Reaction with Metals

   It combines with metals giving silicides.

   For example,

   $$2Mg + Si \longrightarrow Mg_2Si$$

3. Solubility

   It dissolves in aqua regia and alkalies. It gives a silicate on fusion with alkali.

   For example,

   $$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2O$$

4. With Steam

   It decomposes steam as follows:

   $$Si + 2H_2O \longrightarrow SiO_2 + 2H_2$$

5. Ignition

   Amorphous silicon can burn with O_2 and F_2.

   $$Si + O_2 \longrightarrow SiO_2$$

   $$Si + 2F_2 \longrightarrow SiF_4$$

Uses

1. Silicon chips doped with P, As, Al or Ga to enhance the semiconductor properties are used for computing devices.
2. It is used in the manufacture of many alloys with high strength, hardness, resistant power against acids like ferrosilicon, manganese silicon, bronze etc. Ferro-silicon is used to prepare acid resistant steel.

NITROGEN (N_2)

It was discovered by Daniel Rutherford who called it foul air or mephitic air (killer of life). Lavoisier established its elemental nature and called it Azote (means without life). The name nitrogen was derived from nitre in which nitrogen element is present.

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CHLORINE

It was discovered by Scheele and named by Davy.

Occurrence

It occurs in combined state mainly in nature in the form of following chloride ores:

Sea water: [NaCl]

Carnalite: $MgCl_2.KCl.6H_2O$

Horn Silver: AgCl

Sylvine: KCl

Chlorapatite: $3Ca_3(PO_4)_2.CaCl_2$

Preparation

1. By the Oxidation of Hydrochloric Acid
Hydrochloric acid can be oxidized into chlorine by using any of these oxidants MnO_2, $KMnO_4$, $K_2Cr_2O_7$, O_3, Pb_3O_4, PbO_2, etc.

$$HCl + \text{oxidizing agent} \longrightarrow Cl_2\uparrow$$

For example,

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

$$Pb_3O_4 + 8HCl \longrightarrow 2PbCl_2 + 4H_2O + Cl_2$$

$$NaClO + 2HCl \longrightarrow NaCl + H_2O + Cl_2$$

2. From Metal Chlorides
When any metal chloride is heated with conc. H_2SO_4 in presence of MnO_2, chlorine is formed as follows:

$$MCl + MnO_2 + \text{conc. } H_2SO_4 \xrightarrow{\Delta} Cl_2\uparrow$$

For example,

$$2NaCl + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2\uparrow$$

3. Laboratory Method
In lab, chlorine is formed as follows:

(i) By the oxidation of HCl using MnO2: When concentrated HCl is heated with MnO_2 in a round bottom flask, chlorine is formed.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

(ii) By the oxidation of HCl using $KMnO_4$: When cold and concentrated HCl is treated with $KMnO_4$, chlorine is formed.

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

In both these methods, chlorine is first passed through water and then through concentrated H_2SO_4 to remove HCl gas and water vapours, respectively. Here, chlorine is collected by upward displacement of air method.

4. From Platinic Chloride or Gold Chloride
When these are heated in a hard glass tube, pure chlorine is obtained as follows:

$$PtCl_4 \xrightarrow{647\text{ K}} PtCl_2 + Cl_2 \xrightarrow{855\text{ K}} Pt + 2Cl_2$$

$$2AuCl_3 \xrightarrow{448\text{ K}} 2AuCl + 2Cl_2 \xrightarrow{458\text{ K}} 2Au + 3Cl_2$$

5. Deacon's Method
Here chlorine can be obtained by the oxidation of HCl by air in presence of catalyst cupric chloride at 400–450°C.

$$\underset{\substack{\text{air}\\4:1}}{4HCl + O_2} \xrightarrow{CuCl_2} Cl_2 + 2H_2O$$

Here, the catalytic action of cupric chloride can be explained by the mechanism given as under.

$$2CuCl_2 \xrightarrow{\text{High temp.}} Cu_2Cl_2 + Cl_2$$

$$2Cu_2Cl_2 + O_2\text{ (air)} \longrightarrow \underset{\text{Copper oxychloride}}{2Cu_2OCl_2}$$

$$Cu_2OCl_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O$$

Here, chlorine is associated with HCl, air (O_2, N_2) and steam. From it HCl and water can be removed by passing it through washing tower and drying tower, respectively. Now chlorine has impurities of O_2 and N_2. Cl_2 is made moisture free by conc. H_2SO_4.

6. By the Electrolysis of Brine Solution
Cl_2 is also prepared by the electrolysis of brine (aq NaCl) at anode by using Nelson, Castner-Kelner or Salvey cell etc.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

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4. Oxidizing and Bleaching Agent
   Br_2 acts as an oxidizing agent and a bleaching agent as it generates nascent oxygen as follows:

$$Br_2 + H_2O \longrightarrow HBr + HOBr \xrightarrow{\Delta} HBr + [O]$$

It can oxidize KI into iodine.

$$2KI + Br_2 \longrightarrow 2KBr + I_2$$

It can oxidize sulphites into sulphates

$$Na_2SO_3 + Br_2 + H_2O \longrightarrow Na_2SO_4 + 2HBr$$

It can oxidize thiosulphate into sulphate.

$$Na_2S_2O_3 + Br_2 + H_2O \longrightarrow Na_2SO_4 + S + 2HBr$$

It can oxidize arsenites into arsenates.

$$Na_3AsO_3 + Br_2 + H_2O \longrightarrow Na_3AsO_4 + 2HBr$$

It can oxidize hydrogen sulphide into sulphur.

$$H_2S + Br_2 \longrightarrow 2HBr + S$$

It can oxidize SO_2 into H_2SO_4.

$$SO_2 + Br_2 + 2H_2O \longrightarrow 2HBr + H_2SO_4$$

5. With Ammonia
   Bromine reacts with ammonia as follows:

$$\underset{\text{Excess}}{NH_3} + 3Br_2 \longrightarrow NBr_3 + 3HBr$$

$$\underset{\text{Excess}}{8NH_3} + 3Br_2 \longrightarrow 6NH_4Br + N_2$$

6. With Mercuric Oxide
   It reacts with mercuric oxide to give mercury oxybromide. However, if bromine vapours are passed over dry HgO at 333 K, Br_2O is formed.

$$2HgO + 2Br_2 + H_2O \longrightarrow \underset{\text{Mercury oxybromide}}{HgBr_2.HgO} + 2HBrO$$

$$HgO + 2Br_2 \longrightarrow \underset{\text{Bromine monoxide}}{Br_2O} + HgBr_2$$

7. With Organic Compounds
   It gives addition and substitution reactions with organic compounds (hydrocarbons) as follows:

$$C_2H_4 + Br_2 \longrightarrow C_2H_4Br_2$$

$$C_2H_6 + Br_2 \longrightarrow C_2H_5Br + HBr$$

Uses

1. It is used to prepare tetra ethyl lead (TEL) a famous antiknocking substance.

$$C_2H_6 + Br_2 \xrightarrow{hv} C_2H_5Br + HBr$$

$$4C_2H_5Br + 4Na - Pb \longrightarrow (C_2H_5)_4Pb + 4NaBr + 3Pb$$

2. AgBr is used in photography.
3. The major use of bromine is in the manufacture of ethylene bromide which is used as an additive to leaded petrol (antiknock gasoline component).
4. It is also used to prepare bromine water, dyes, drugs, AgBr, benzyl bromide (tear gas) etc.
5. It is used as a germicide, oxidizing and bleaching agent.

IODINE (I_2)

It was discovered by Courtios and named by Gay Lussac (iodi means violet). It is the rarest halogen with metallic lusture.

Occurrence

It is present in combined state in the form of salts like iodides, iodates etc.

Main Source

The main sources of iodine are

(i) Kelp (ash of sea weeds like Laminaria) 1% metal iodide
(ii) Caliche or Crude chile salt petre: $NaIO_3$ (0.2 %)

Preparation

1. From Kelp
   On commercial scale iodine is prepared from kelp which are the ashes of sea weeds like laminaria. Kelp has many salts of Na and K like chlorides, carbonates, sulphates and iodides. Here, iodides are in solution. When this solution (mother liquor) is heated with concentrated sulphuric acid in presence of MnO_2 in iron retorts, I_2 is formed which is sublimated in pure form.

$$2NaI + 3H_2SO_4 + MnO_2 \xrightarrow{\Delta} 2NaHSO_4 + MnSO_4 + 2H_2O + I_2\uparrow$$

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(c) A solution of KHF_2 in KF
(d) A molten mixture of $Ca_3(PO_4)_2.CaF_2$ and cryolite

36. Boro and silicon resemble in all respects except
(a) both form halides which are Lewis acids.
(b) their chlorides hydrolyze to their respective acids.
(c) both form acidic oxides.
(d) their hydrates are stable.

37. Fluorine shows only one oxidation state (−1) because it has
(a) a small covalent radius
(b) a low bond energy
(c) a high electronegativity
(d) no d-orbital available for bonding

38. Which of the following properties is not exibited by nitrogen?
(a) Supporter of life
(b) Catenation
(c) Low boiling point
(d) Hydrogen bonding

39. Which of the following halogens is extracted from sea-weeds?
(a) I_2 (b) Cl_2
(c) F_2 (d) Br_2

40. $Na_2S_2O_3$ is reduced by I_2 to:
(a) Na_2SO_4 (b) $NaHSO_3$
(c) Na_2S (d) $Na_2S_4O_6$

41. Fluorine reacts with H_2S to produce:
(a) S and HF (b) SF_2
(c) SF_6 (d) SF_4

42. Which of the following has least bond energy?
(a) H_2 (b) F_2
(c) O_2 (d) N_2

43. The element evolving two different gases on reaction with conc. sulphuric acid is
(a) S (b) C
(c) Sn (d) P

44. Chlorine acts as an oxidizing agent when it reacts with:
(a) $Fe_2(SO_4)_3$ (b) O_3
(c) $KMnO_4$ (d) $FeSO_4$

45. The most reactive and least reactive forms of phosphorous are respectively:
(a) White and black phosphorous
(b) White and red phosphorous
(c) Red and white phosphorous
(d) Scarlet and red phosphorous

46. Which of the following noble gases is the most polarized?
(a) Xenon (b) Radon
(c) Helium (d) Krypton

47. The electrolysis of brine produces:
(a) NaOH and $NaClO_3$
(b) NaCl and NaClO
(c) Only Cl_2
(d) Cl_2 and NaOH

48. Diamond is hard because
(a) All the four valence electrons are bonded to each carbon atoms by covalent bonds.
(b) It is a giant molecule.
(c) It is made up of carbon atoms.
(d) It cannot be burnt.

49. Which of the following noble gases is the least polarized?
(a) Krypton (b) Radon
(c) Helium (d) Xenon

50. The high oxidizing power of fluorine is due to
(a) low heat of dissociation and high heat of hydration.
(b) high heat of dissociation and high heat of hydration.
(c) high electron affinity.
(d) high heat of dissociation and low heat of hydration.

51. Fluorine reacts with aqueous $KClO_3$ to produce
(a) KCl (b) $KClO_4$
(c) KClO (d) $KClO_2$

52. Deep-sea divers breathe using a mixture of
(a) O_2 and He (b) O_2 and H_2
(c) O_2 and Ar (d) O_2 and Kr

53. Which one of the following pairs is obtained on heating ammonium dichromate?
(a) N_2 and H_2O (b) NO and NO_2
(c) N_2O and H_2O (d) NO_2 and H_2O

54. In the manufacture of bromine from sea water, the mother liquor containing bromides is treated with
(a) chlorine (b) iodine
(c) sulphur dioxide (d) carbon dioxide

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(c) 30 pentagons and 20 hexagons.
(d) 24 pentagons and 36 hexagons.

92. In which of the following reactions is Cl_2 (gas) produced?
(a) $KCl + Br_2 \longrightarrow$
(b) $NaCl + K_2Cr_2O_7 +$ conc. $H_2SO_4 \longrightarrow$
(c) $NaOCl + NH_3 \longrightarrow$
(d) $Ca(OCl)Cl + H_2O \longrightarrow$

93. Helium is suitable for low temperature gas thermometry because of its
(a) High boiling point and high polarizability.
(b) Low boiling point and near-ideal behaviour.
(c) High transition temperature.
(d) Real behaviour.

94. Phosphorous is obtained by the reduction of phosphate rock using
(a) Al at high temperature.
(b) Coke and silica at high temperature.
(c) Silica at high temperature.
(d) Fe_2O_3 and coke at high temperature.

95. Very pure silicon is prepared by
(a) Heating SiO_2 with KF.
(b) The electrolysis of SiO_2 in SiF_4.
(c) Reducing pure silicon tetrachloride with magnesium.
(d) Decomposing $K_2[SiF_6]$.

96. $NaHSO_4$ reacts with F_2 to produce mainly
(a) $Na_2S_2O_5$ (b) $Na_2S_2O_8$
(c) $Na_2S_2O_3$ (d) $Na_2S_2O_7$

97. Very pure silicon is an insulator, but becomes a p-type or an n-type semiconductor when doped with a
(a) Group 12 and a group 16 element, respectively
(b) Group 4 and group 6 element, respectively
(c) Group 1 and a group 12 element, respectively
(d) Group 13 and a group 15 element, respectively

98. Chlorine can be manufactured by the oxidation of HCl in air in the presence of a $CuCl_2$ catalyst at 450°C. The process is known as the
(a) Nelson process
(b) Deacon process
(c) Solvay process
(d) Chloride process

99. White phosphorous reacts with calcium to form a certain compound which, on hydrolysis, produces
(a) P_4O_6 (b) P_4O_{10}
(c) PH_3 (d) P_2H_4

100. Cl_2 reacts with dilute NaOH and concentrated NaOH to, respectively produce
(a) $NaClO_3$ and NaClO
(b) NaClO and $NaClO_2$
(c) NaCl and $NaClO_4$
(d) NaClO and $NaClO_3$

Multiple Correct Answer Type Question (More Than One Choice)

101. Which of the following halogens does not turn starch iodine paper blue?
(a) I_2 (b) F_2
(c) Cl_2 (d) Br_2

102. Iodine reacts with hypo to give
(a) Na_2S (b) NaI
(c) Na_2SO_3 (d) $Na_2S_4O_6$

103. Electrolysis of aqueous solution of Brine (NaCl) gives
(a) O_2 (b) NaOH
(c) H_2 (d) Cl_2

104. Cl_2 reacts with hot aqueous NaOH to give
(a) NaClO (b) $NaClO_4$
(c) NaCl (d) $NaClO_3$

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(R): There is a repulsion operating between the nonbonding 2p electrons on the bonded F-atoms.

148. (A): In presence of moisture, Cl_2 can act as an oxidant and bleaching agent.

(R): Chlorine reacts with moisture to give HCl and HClO. HClO being less stable decomposes to give nascent oxygen.

149. (A): Deep sea divers use heliumoxygen mixture for respiration.

(R): Helium is inert in nature.

150. (A): Iodine is liberated when KI is added to a solution of Cu^{2+} ions but Cl_2 is not liberated when KCl is added to a solution of Cu^{2+} ions.

(R): I^- ions are strong reducing agent whereas as Cl^- ions does not act as reducing agent.

151. (A): Bond strengths in the nitrogen, oxygen and fluorine molecules follow the order $N_2 > O_2 > F_2$.

(R): The electronegativity increases in the order N < O < F.

152. (A): Fluorine acts as a stronger oxidizing agent than oxygen.

(R): Fluorine is more electronegative than oxygen.

153. (A): Iodine is less soluble in water.

(R): It becomes more soluble in presence of KI due to the formation of KI_3.

154. (A): In S_8 molecule, each S atom is bonded to two S atoms.

(R): Each S atom is S_8 molecules is sp^3 hybridized, having two lone pairs of electrons and bonded to two other S-atoms.

155. (A): Iodine shows oxidation state of +1 and +3 in the compounds ICl and ICl_3, respectively.

(R): Iodine coming below the halogens F, Cl and Br in the halogen group of elements in the periodic table shows a higher degree of electropositive nature.

Matrix–Match Type Questions

	p	q	r	s
(A)	O	O	O	O
(B)	O	O	O	O
(C)	O	O	O	O
(D)	O	O	O	O

156. Match the following:

Column I (Allotropic form)	Column II (Structure)
A. Engel's sulphur	(p) Crystalline form yellow crystals
B. χ-sulphur	(q) Fibrous or rubber like
C. Rhombic sulphur	(r) Puckered S_8 rings (crown configuration)
D. γ-monoclinic	(s) S_4 rings, chair conformation, unstable

157. Match the following:

Column I	Column II
A. Boron	(p) Amphoteric oxide
B. Carbon	(q) Acidic oxide
C. Silicon	(r) Catenation
D. Phosphorous	(s) Allotropy

158. Match the following:

Column I	Column II
A. F_2	(p) Metallic lusture
B. Cl_2	(q) Most electronegative
C. Br_2	(r) Highest bond energy
D. I_2	(s) Reddish liquid

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Two adjacent layers are bonded by *p* electron interactions.

On the other hand, Si does not form graphite like structure because

(i) The size of Si atom is larger than that of carbon. The overlap of two 3p orbitals results in poor overlap and hence a weaker bond

(ii) The catenation tendency to form ring structure by Si atom is very small because Si–Si bond energy is lower than C–C bond energy.

Questions For Self Assessment

13. Given reasons for the following:

(i) Carbons acts as an abrasive and also as a lubricant.

[*IIT 1981*]

(ii) Sulphur melts to a clear mobile liquid at 119°C, but on further heating above 160°C, it becomes viscous.

[*IIT 1981*]

(iii) Graphite is used as a solid lubricant.

[*IIT 1985*]

14. Give reasons for the following:

(i) Fluorine cannot be prepared from fluorides by chemical oxidation.

[*IIT 1985*]

(ii) Valency of oxygen is generally two, whereas sulphur shows valency of two, four and six.

[*IIT 1988*]

(iii) Bond dissociation energy of F_2 is less than that of Cl_2.

[*IIT 1992*]

15. (i) Give reasons why elemental nitrogen exists as a diatomic molecule whereas elemental phosphorous as a tetraatomic molecule.

[*IIT 2000*]

(ii) The O–O bond energy is less than the S–S bond energy. Explain.

16. (i) Write the two resonance structures of ozone which satisfy the octet rule.

(ii) O_2 is inert room temperature. Why?

(iii) Red phosphorus is denser and chemically less reactive than white phosphorus. Why?

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$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO + H_2O_2$$

$$2Na_2O_2 + 2H_2SO_4 \xrightarrow{\Delta} 2Na_2SO_4 + 2H_2O + O_2$$

5. As a Powerful Oxidizing Agent

Being a strong oxidizing agent it oxidizes chromic compounds into chromates and sulphides into sulphates etc.

$$3Na_2O_2 + 3H_2O_2 \longrightarrow 6NaOH + 3[O]$$

$$2Cr(OH)_3 + 4NaOH\ 3[O] \longrightarrow 2Na_2CrO_4 + 5H_2O$$

$$2Cr(OH)_3 + 3Na_2O_2 \longrightarrow 2Na_2CrO_4 + 2NaOH + 2H_2O$$

$$\underset{\text{Benzoyl chloride}}{2C_6H_5COCl} + Na_2O_2 \longrightarrow \underset{\text{Benzoyl peroxide}}{(C_6H_5CO)_2O_2} + 2NaCl$$

6. Action of CO and CO_2

It reacts with carbon monoxide and carbon dioxide to form sodium carbonate as follows:

$$Na_2O_2 + CO \longrightarrow Na_2CO_3$$

$$2Na_2O_2 + 2CO_2 \longrightarrow 2Na_2CO_3 + O_2$$

Uses

1. As it readily combines with CO and CO_2, it is used for the purification of air in submarines, diving bells and other confined spaces.
2. It is used as an oxidizing agent.
3. It is also used for bleaching straw, silk etc., in the form of soda bleach (Na_2O_2 + dil. HCl) i.e., oxone.
4. It is used in the preparation of dyes and some other chemicals like benzoyl peroxide, sodium per borate etc.

Caustic Soda or Sodium Hydroxide (NaOH)

Methods of Preparation

It is prepared by the following methods:

Gossage or Causticization Method

In this method a suspension of lime [CaO + $Ca(OH)_2$] is treated with sodium carbonate to obtain NaOH as follows:

$$\underset{\text{(aq.)}}{Na_2CO_3} + \underset{\text{(aq.)}}{Ca(OH)_2} \longrightarrow 2NaOH + \underset{\text{(aq.)}}{CaCO_3}$$

From here, calcium carbonate can be easily separated and caustic soda solution can be easily drained out and evaporated to dryness to obtain in crystalline form. This NaOH is not pure and has impurities like $CaCO_3$, Na_2CO_3, $Ca(OH)_2$ etc.

Lowig's Method

Here a mixture of sodium carbonate and ferric oxide is heated in a revolving furnace upto redness to get sodium ferrite which is first of all cooled and hydrolyzed by hot water into NaOH solution and in soluble ferric oxide. The solution is filtered and evaporated upto dryness to get the flacks of NaOH.

$$Na_2CO_3 + Fe_2O_3 \xrightarrow[-CO_2\uparrow]{\text{Fussion}} 2NaFeO_2$$

$$2NaFeO_2 \xrightarrow[\Delta]{H_2O} 2\ NaOH + Fe_2O_3$$

- In both Gossage and Lowig's method, the initial material is sodium carbonate.

Modern Method or By Electrolysis of Brine Solution (aq. NaCl)

For the electrolysis of aqueous NaCl electrolytic cells like Nelson, Castner–Kelner, Salvay cells are used. Here NaOH, Cl_2, H_2 are formed.

Reactions

$$NaCl \longleftrightarrow Na^+ + Cl^-$$

$$H_2O \longleftrightarrow H^+ + OH^-$$

At Anode

$$2Cl^- \longleftrightarrow Cl_2 + 2e^-$$

At Cathode

$$2Na^+ + 2e^- \longrightarrow 2Na$$

$$2Na + 2H.OH \longrightarrow 2NaOH + H_2\uparrow$$

- As here chlorine can react with NaOH solution even in cold hence it is necessary that it must be kept away from NaOH by using a porous diaphragm or by using a mercury cathode so that this reaction can be checked.

$$2NaOH + Cl_2 \longrightarrow NaClO + NaCl + H_2O$$

3. Heating Effect

On heating it changes into anhydrous sodium carbonate as follows:

$$Na_2CO_3.10H_2O \xrightarrow{-10\,H_2O} Na_2CO_3 \xrightarrow[\text{Strong}]{\Delta} X$$

4. With Acids

It is easily decomposed by acids as follows:

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2 \uparrow$$

5. With CO_2

When CO_2 is passed through the concentrated solution of sodium carbonate, sodium bicarbonate gets precipitated.

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2NaHCO_3$$

6. With Silica

When it is treated with silica it gives sodium silicate as follows:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2 \uparrow$$

Sodium silicate is known as water glass or soluble glass as it dissolves in water.

7. With Sulphur and Sulphur dioxide

When aqueous solution of sodium carbonate is treated with sulphur dioxide and sulphur, sodium thiosulphate is formed.

$$Na_2CO_3\,(aq) + SO_2 \longrightarrow Na_2SO_3 + CO_2$$

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

8. With Salts of NonAlkali Metals

It reacts with salts of nonalkali metals to form insoluble normal or basic carbonates as follows:

(a) **With Lead Acetate:** When it is treated with lead acetate it gives basic lead carbonate as follows:

$$3(CH_3COO)_2Pb + 3Na_2CO_3 + H_2O \longrightarrow \underset{\text{Basic lead carbonate}}{2PbCO_3Pb(OH)_2} + CO_2 + 6CH_3COONa$$

(b) **Reaction with Copper Sulphate:** When it is treated with copper sulphate it gives basic copper carbonate as follows:

$$2CuSO_4 + 2Na_2CO_3 + H_2O \longrightarrow \underset{\text{Basic copper carbonate}}{Cu(OH)_2\,CuCO_3} + CO_2 + Na_2SO_4$$

(c) **With Zinc Sulphate:** When it is treated with zinc sulphate it gives basic zinc carbonate as follows:

$$5ZnSO_4 + 5Na_2CO_3 + 4H_2O \longrightarrow \underset{\text{Basic zinc carbonate}}{[3Zn(OH)_2\,2ZnCO_3].H_2O} + 3CO_2 + 5Na_2SO_4$$

(d) Carbonates of some metals like Fe, Al, Sn undergo hydrolysis at once into hydroxides as follows:

$$Fe_2(SO_4)_3 + 3Na_2CO_3 \longrightarrow Fe_2(CO_3)_3 + 3Na_2SO_4$$

$$Fe_2(CO_3)_3 + 3H_2O \longrightarrow 2Fe(OH)_3 + 3CO_2$$

Uses

1. It is used for softening hard water, refining of petrol and in the manufacture of glass, borax etc.
2. $Na_2CO_3 + K_2CO_3$ is a fusion mixture hence it is used in quantitative and qualitative analysis.
3. It is used for washing purpose in laundry.
4. It is used in paper, textile and paint industries.
5. Na_2CO_3 gives pink colour with HPH, yellow colour with MeOH or methyl red and blue colour with red litmus.

Sodium Bicarbonate or Baking Soda ($NaHCO_3$)

Preparation

It is prepared by passing carbon dioxide through a saturated solution of sodium carbonate as follows:

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$$

2. Its mixture with Na_2CO_3 can be used as a fusion mixture in laboratory.

Potassium Bicarbonates ($KHCO_3$)

Preparation

It is prepared by passing CO_2 through cold saturated solution of K_2CO_3.

$$K_2CO_3 + H_2O + CO_2 \longrightarrow 2KHCO_3$$

Physiochemical Properties

1. It is in the form of white powder.
2. Chemically, it resembles $NaHCO_3$ except that it is more soluble in water.

Uses

It is used in making powder and medicines.

Potassium Chloride (KCl)

Occurrence: It occurs as sylvine (KCl) and as carnalite ($KCl.MgCl_2.6H_2O$).

Preparation

From Sylvine (KCl)

It is a mixture of KCl and NaCl. When the boiling hot saturated solution of the mixed salts in water is cooled, KCl separates out and NaCl is left behind in the solution.

From Carnalite ($KCl.MgCl_2.6H_2O$)

It is always found mixed with NaCl and $MgSO_4$. To remove NaCl and $MgSO_4$, the ore is grounded and extracted with a hot 20% solution of $MgCl_2$. Carnalite dissolves while NaCl and $MgSO_4$ remain undissolved. These are filtered off and the solution which contains only carnalite is crystallized so that cubic crystals of KCl separate out leaving behind $MgCl_2$ in the solution.

Physiochemical Properties

1. It is a colourless crystalline solid having cubic crystals.
2. Its melting point and boiling point are 768°C and 1411°C, respectively.
3. It is extremely soluble in water and closely resembles NaCl in most of its properties, except that its solubility increases rapidly with the temperature and is more readily fusible.

Uses

1. It is used in the manufacture of potassium and its compounds.
2. It is used as a potassium fertilizer (K-type fertiliser), since it supplies potassium (as K_2O) to the soil.

Potassium Iodide KI

Preparation

1. When ferroso–enferric iodide and potassium carbonate are treated as follows, potassium iodide is formed.

$$4K_2CO_3 + Fe_3I_8 + 4H_2O \longrightarrow 8KI + 4CO_2 + \underset{\text{ppt.}}{Fe(OH)_2.2Fe(OH)_3}$$

From here the precipitate can be easily filtered off and the solution on crystallization gives the crystals of KI.

2. When KOH or K_2CO_3 are treated with HI, KI is formed as follows:

$$KOH + HI \longrightarrow KI + H_2O$$

$$K_2CO_3 + 2HI \longrightarrow 2KI + CO_2 + H_2O$$

3. When iodine is heated with hot and conc. solution of KOH, KI and KIO_3 solution is formed which is evaporated to dryness and the obtained solid residue is ignited with powdered charcoal to obtained KI as follows:

$$3I_2 + 6KOH \longrightarrow 5KI + KIO_3 + 3H_2O$$

$$KIO_3 + 3C \longrightarrow KI + 3CO$$

Physiochemical Properties

1. It is a white crystalline solid which is highly soluble in water and alcohol.
2. It dissolves free iodine and forms KI_3.

$$KI + I_2 \longrightarrow \underset{\text{Unstable}}{KI_3}$$

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4. It is used for filing rubber.
5. When it is mixed with asbestos it can be used as an insulator for steam pipes and boilers.

Magnesium Hydroxide $Mg(OH)_2$

$Mg(OH)_2$ occurs in nature as brucite.

Preparation

1. From MgO

It is prepared by dissolving MgO into water as follows:

$$MgO + H_2O \longrightarrow Mg(OH)_2$$

2. By Treating Magnesium Salt with Alkali

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCl_2$$

$$MgCl_2 + 2NaOH \longrightarrow Mg(OH)_2 + 2NaCl$$

Physiochemical Properties

1. It is a white powder and partially soluble in water.
2. It is a basic oxide and forms salts with acids.
3. On heating, $Mg(OH)_2$ decomposes to form MgO.
4. It dissolves in ammonium chloride solution forming a complex ion. It partly explains why magnesium does not precipitate with the hydroxides of Al, Cr and Fe in IIIrd group of qualitative analysis.

$$Mg(OH)_2 + 2NH_4Cl \longrightarrow MgCl_2 + 2NH_4OH$$

Uses

1. $Mg(OH)_2$ is an aqueous suspension used in medicines as an antacid, called 'Milk of Magnesia'.

Magnesium Carbonate ($MgCO_3$)

$MgCO_3$ occurs in nature as dolomite, $MgCO_3.CaCO_3$ and as magnesite $MgCO_3$.

Preparation

1. By Treating an aqueous solution of magnesium salt with $NaHCO_3$

$$MgSO_4 + 2NaHCO_3 \longrightarrow MgCO_3 + Na_2SO_4 + H_2O + CO_2$$

2. By passing CO_2 through suspension of MgO in water

$$MgO + H_2O + 2CO_2 \longrightarrow Mg(HCO_3)_2$$

$$Mg(HCO_3)_2 + MgO \longrightarrow 2MgCO_3 + H_2O$$

3. From Magnesium Sulphate and Sodium Carbonate

It cannot be directly obtained by the reaction of these two as a white precipitate of basic magnesium carbonate or magnesium alba is obtained first which is suspended in water and CO_2 is passed into it to obtain magnesium bicarbonate (fluid magnesium) whose solution on boiling gives magnesium carbonate.

$$2MgSO_4 + 2Na_2CO_3 + H_2O \longrightarrow MgCO_3\,Mg(OH)_2 + 2Na_2SO_4 + CO_2$$

$$MgCO_3\,Mg(OH)_2 + 3CO_2 + H_2O \longrightarrow 2Mg(HCO_3)_2$$

$$Mg(HCO_3)_2 \longrightarrow MgCO_3 + CO_2 + H_2O$$

Physiochemical Properties

1. It is a white solid powder which is insoluble in water.
2. On suspension in water and by passing CO_2 it forms $Mg(HCO_3)_2$.

$$MgCO_3 + H_2O + CO_2 \longrightarrow \underset{\text{Magnesium bicarbonate}}{Mg(HCO_3)_2}$$

3. With Acids

It dissolves in acids giving salts as follows:

$$MgCO_3 + H_2SO_4 \longrightarrow MgSO_4 + H_2O + CO_2$$

$$MgCO_3 + 2HCl \longrightarrow MgCl_2 + H_2O + CO_2$$

4. Heating Effect

$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$$

Uses

1. $(MgCO_3)_x\,[Mg(OH)_2].3H_2O$ (magnesium alba) is used in tooth powder as an antacid and laxative.
2. It is also used in the manufacturing of glass, ceramics etc.

On heating with chlorine, slaked lime gives bleaching powder.

$$Ca(OH)_2 \xrightarrow[30^\circ C]{Cl_2} \underset{\text{Bleaching powder}}{CaOCl_2}$$

When it is heated with chlorine upto redness or with NH_4Cl, calcium chloride is formed.

$$Ca(OH)_2 \xrightarrow{Cl_2 \text{ red hot}} CaCl_2$$

$$Ca(OH)_2 \xrightarrow{NH_4Cl} CaCl_2 + NH_3$$

Uses

1. It is used in softening of water, purification of coal gas, sugar etc.
2. It is used in the manufacturing of bleaching powder, sodium carbonate etc.
3. It is also used in making of mortar and plaster used as building materials.

Calcium Oxide or Marble or Lime Stone ($CaCO_3$)

In nature it occurs as lime stone, ice land spar, marble and shells of sea animals.

Preparation

Laboratory Method

In laboratory it is prepared by passing CO_2 through lime water or by adding sodium carbonate solution into calcium chloride as follows:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$

Physiochemical Properties

1. It is a white solid and which is almost insoluble in water.
2. **Heating effect:**

$$CaCO_3 \xrightarrow{1000^\circ C} CaO + CO_2$$

3. **With dilute acids:**

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2 \uparrow$$

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2 \uparrow$$

Uses

1. It is used in the preparation of cement, washing soda ($NaHCO_3$ by Solvay method).
2. In the extraction of many metals like iron.
3. Marble in used as a building material.
4. Precipitated chalk is used in the manufacture of paints, medicines and tooth paste etc.

Calcium Sulphate Dihydrate or Gypsum ($CaSO_4.2H_2O$)

Calcium sulphate occurs as anhydride ($CaSO_4$) and gypsum ($CaSO_4.2H_2O$). Naturally occurring calcium sulphate is called alabaster.

Preparation

In laboratory it is prepared by the reaction of calcium carbonate and calcium chloride with dilute acids as follows:

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2 \uparrow$$

$$CaCl_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HCl$$

$$CaCl_2 + Na_2SO_4 \longrightarrow CaSO_4 + 2NaCl$$

Physiochemical Properties

1. It is a white crystalline solid which is partially soluble in water and its dissolution in water is exothermic.
2. It also dissolves in dilute acids, ammonium sulphate etc.
3. Heating Effect: On heating, gypsum gives plaster of paris (Calcium sulphate hemihydrate). Plaster of Paris when mixed with water, gives a hard mass with light expansion. Gypsum on heating at 200°C gives anhydrous calcium sulphate known as dead burnt plaster.

$$2CaSO_4\ 2H_2O \underset{\text{Setting } (\Delta H = -Ve)}{\overset{120^\circ C}{\rightleftharpoons}} \underset{\text{Plaster of Paris}}{(CaSO_4)_2\ H_2O} + 3H_2O$$

$$\downarrow \Delta,\ 200^\circ C$$

$$\underset{\text{Dead burnt plast}}{2CaSO_4 + H_2O}$$

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3. In alum crystals, 6 water molecules are held by monovalent ion, 6 water molecules are held by trivalent ion, 12 water molecules are held in the crystal structure.
4. Aqueous solutions of alum are acidic due to cationic hydrolysis of trivalent cation.
5. Feature alum or Hair-salt $Al_2SO_4.18H_2O$ is a native form of aluminium sulphate.
6. On heating an alum at high temperature the alum swells up into a porous mass which is called burnt alum.
7. Alums act as coagulants as they are effective in precipitating colloids.
8. Alums have germicide properties.

Potash Alum $K_2SO_4.Al_2(SO_4)_3.24H_2O$

Preparation

1. From Bauxite or Aluminium Sulphate

When bauxite is boiled with sulphuric acid solution of aluminium sulphate is obtained. In it K_2SO_4 is added in a calculated amount followed by concentration and cooling to get the crystals of alum.

$$Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$$

$$Al_2(SO_4)_3 + K_2SO_4 + 24H_2O \longrightarrow \underset{\text{Potash alum}}{K_2SO_4.Al_2(SO_4)_3.24H_2O}$$

2. From Alunite or Alum Stone

It is boiled with dilute sulphuric acid and a calculated amount of K_2SO_4 is added in the boiled solution, the resultant solution on cooling gives the crystals of alum.

$$\underset{\text{Alum stone}}{K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3} + 6H_2SO_4 \longrightarrow K_2SO_4 + 3Al_2(SO_4)_3 + 12H_2O$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow K_2SO_4 Al_2(SO_4)_3.24H_2O$$

Physiochemical Properties

1. It is a white crystalline solid compound.
2. It is soluble in water and the aqueous solution is acidic due to cationic hydrolysis of $Al_2(SO_4)_3$. The aqueous solution has K^+, Al^{3+} and SO_4^{2-}.
3. Heating Effect: On heating it swells up due to elimination of water molecules as follows:

$$K_2SO_4.Al_2(SO_4)_3.14H_2O \xrightarrow{473\text{ K}} K_2SO_4 Al_2(SO_4)_3 + 24H_2O$$

$$K_2SO_4.Al_2(SO_4)_3 \xrightarrow{\text{Red hot}} K_2SO_4 + Al_2O_3 + 3SO_3$$

Uses of Alums

1. As mordent in dyeing.
2. As a syptic to stop bleeding.
3. In tanning of leather.
4. In purification of water (negative impurities in water).
5. It is used in sizing of cheap quality paper.

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42. The hydration energy of Mg^{2+} ions is higher than that of

(a) Al^{3+} (b) Be^{2+}
(c) Na^{+} (d) None of these

43. Plaster of Paris hardens by

(a) changing into CaO
(b) giving out water
(c) utilizing water
(d) giving off CO_2

44. An $FeCl_3$ solution reacts with sodium hydroxide to produce

(a) Fe_3O_4 (b) $Fe_2O_3.nH_2O$
(c) Fe_2O_3 and FeO (d) FeO and $FeCl_3$

45. Which of the following set of raw materials are used in the manufacturing of Na_2CO_3 by Solvay process?

(a) $CaCl_2$, NH_3, CO_2
(b) NaOH, NH_3, CO_2
(c) NaCl, NH_3, CO_2
(d) $Ca(OH)_2$, NH_3, CO_2

46. In which of these pairs both species are soluble in NaOH solution?

(a) $Pb(OH)_2$, $Sn(OH)_4$
(b) $Al(OH)_3$, $Fe(OH)_3$
(c) $Zn(OH)_2$, $Cu(OH)_2$
(d) $Cr(OH)_2$, $Sn(OH)_2$

47. A burning strip of magnesium is introduced into a jar containing a gas. After sometime, the walls of the container is coated with carbon. The gas in the container is

(a) H_2O (b) CO_2
(c) O_2 (d) N_2

48. In which of the following pairs, both species on heating do not undergo any chemical change?

(a) $MgCO_3$, $KHCO_3$
(b) Cs_2CO_3, KNO_2
(c) Na_2CO_3, $NaNO_3$
(d) Li_2CO_3, KNO_2

49. Cl_2O_6 on reaction with $Ba(OH)_2$ gives

(a) $BaCl_2O_7$
(b) $Ba(ClO_3)_2 + Ba(ClO_2)_2$
(c) $Ba(Cl_2O_7)_2 + Ba(ClO_2)_2$
(d) $Ba(ClO_3)_2 + Ba(ClO_4)_2$

50. Halides of alkaline earth metals form hydrates such as $MgCl_2.6H_2O$, $CaCl_2.6H_2O$, $BaCl_2.2H_2O$ and $SrCl_2.2H_2O$. This shows that halides of group 2 elements:

(a) can absorb moisture form air.
(b) act as dehydrating agents.
(c) are hydroscopic in nature.
(d) all of the above.

51. Which of the following is correct?

(a) Sodium reduces CO_2 to carbon.
(b) In the Castner's process of sodium extraction, NaCl is used as an electrolyte.
(c) Magnalium is an alloy of Mg and Zn.
(d) Mg reacts with cold water and liberates hydrogen gas.

52. Which hydroxide is insoluble in sodium hydroxide?

(a) $Fe(OH)_3$ (b) $Al(OH)_3$
(c) $Cr(OH)_3$ (d) Both (a) and (c)

53. The metal (M) is prepared by the electrolysis of fused chloride. It reacts with hydrogen to form a colourless solid from which hydrogen is released on treatment with water. The metal (M) is

(a) Ca (b) Al
(c) Zn (d) Cu

54. The magnetic moment of KO_2 at room temperature is

(a) 1.43 BM (d) 2.64 BM
(c) 2.41 BM (d) 1.73 BM

55. When washing soda is heated

(a) CO_2 is released
(b) Water vapour is released
(c) CO_2 is released
(d) $CO + CO_2$ is released

56. Sodium peroxo borate, $Na_2[B_2(O_2)_2(OH)_4]\,6H_2O$ is a constituent of

(a) Bleaching powder
(b) Rocket propellants
(c) Washing powder
(d) Baking powder

57. Solvay process converts which of the following into soda ash?

111. Nitrogen dioxide can be obtained from

(a) $NaNO_3$ (b) $Cu(NO_3)_2$
(c) $AgNO_3$ (d) $Hg(NO_3)_2$

112. Aluminium becomes passive in

(a) $HClO_4$ (b) Conc. HCl
(c) Conc. HNO_3 (d) H_2CrO_4

113. Select the correct statement(s).

(a) Be dissolves in alkali forming $[Be(OH)_4]^{2-}$.
(b) BeF_2 forms complex ion with NaF in which Be goes with cation.
(c) $BeCO_3$ is kept in the atmosphere of CO_2 since, it is least thermally stable.
(d) BeF_2 forms complex ion with NaF in which Be goes with anion.

11 ... hich of the following oxides is/are amphoteric?

Na_2O (b) CaO
(c) Al_2O_3 (d) SnO_2

115. Alkali metals are characterized as

(a) Good conductors of heat and electricity.
(b) High reducing nature.
(c) High melting point.
(d) Solubility in liquid ammonia.

116. Which is true about beryllium?

(a) $Be(OH)_2$ is basic in nature only.
(b) Beryllium halides are electron deficient.
(c) Aqueous solution of $BeCl_2$ is acidic.
(d) It forms unusual carbide Be_2C.

117. The pair of compounds which cannot exist together in aqueous solution is

(a) NaH_2PO_4 and Na_2HCO_3
(b) Na_2CO_3 and $NaHCO_3$
(c) NaOH and NaH_2PO_4
(d) $NaHCO_3$ and NaOH

118. Chemical change can take place in

(a) $K_2CO_3 \xrightarrow{\Delta}$
(b) $Li_2CO_3 \xrightarrow{\Delta}$
(c) $NaHCO_3 \xrightarrow{\Delta}$
(d) $Mg(NO_3)_2 \xrightarrow{\Delta}$

119. Select the correct statements about alkali metals.

(a) All form ionic hydrides (MH).
(b) All form (MNH_2) amide.
(c) All form nitrides.
(d) All form superoxides (MO_2).

120. Which among the following compounds are not paramagnetic?

(a) K_2O_2 (b) NO_2
(c) KO_2 (d) K_2O

121. Which of the following statement is/are correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4?

(a) The vapour when passed into NaOH solution gives a yellow solution of Na_2CrO_4.
(b) A deep red vapour is evolved.
(c) Chlorine gas is evolved.
(d) Chromyl chloride is formed.

122. Nitrate of which of the following elements can be converted into their oxides on heating?

(a) Na (b) Li
(c) Mg (d) Rb

123. Which of the following carbonates can evolve CO_2 on heating?

(a) Na_2CO_3 (b) Rb_2CO_3
(c) Li_2CO_3 (d) $MgCO_3$

124. Sodium sulphate is soluble in water whereas barium sulphate is sparingly soluble because

(a) the hydration energy of sodium sulphate is more than its lattice energy.
(b) the lattice energy of barium sulphate is more than its hydration energy.
(c) the lattice energy has no role to play in solubility.
(d) the hydration energy of sodium sulphate is less than its lattice energy.

125. Which of the following oxides have rock salt structure with coordination number 6 : 6?

(a) MgO (b) CaO
(c) SrO (d) B_2O_3

126. Incorrect match is/are

(a) Soda ash: Na_2CO_3
(b) Pearl ash: $CuCO_3$
(c) Bone ash: K_2CO_3
(d) Baking soda: $NaHCO_3$

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(R): The alkali metals have low electronegativity, their hydrides conduct electricity when fused and liberate hydrogen at the anode.

163. (A): Sodium reacts with oxygen to form Na_2O_2 whereas potassium reacts with oxygen to form KO_2.

(R): Potassium is more reactive than sodium.

164. (A): Crystals of $NaHCO_3$ and $KHCO_3$ show hydrogen bonds of different kinds.

(R): In $NaHCO_3$, the bicarbonate ions are linked in an infinite chain while in $KHCO_3$, a dimeric chain is formed.

165. (A): MgO is used for lining of steel making furnace.

(R): It is a acidic flux and helps in removing basic impurities.

166. (A): When hot and concentrated NaOH reacts with chlorine, NaCl and NaClO are formed.

(R): It is a case of disproportion or autoredox reaction.

167. (A): $BeCl_2$ fumes in moist air.

(R): $BeCl_2$ reacts with moisture to form HCl gas.

168. (A): Magnesium metal burns in air to give a white ash and this ash gives smell of ammonia in contact with water.

(R): The ash contains magnesium nitride also which is hydrolyzed by water and ammonia is evolved.

169. (A): Magnesium is extracted by the electrolysis of fused mixture of $MgCl_2$, NaCl and $CaCl_2$.

(R): Calcium chloride acts as a reducing agent.

170. (A): Alkali metals dissolve in liquid ammonia to give blue solutions.

(R): Alkali metals in liquid ammonia give solvated species of the type

$[M(NH_3)_n]^+$ (M = alkali metals)

[*IIT 2007*]

Matrix-Match Type Questions

	p	q	r	s
(A)	O	O	O	O
(B)	O	O	O	O
(C)	O	O	O	O
(D)	O	O	O	O

171. Match the following:

Column I	Column II
A. Sorel's cement	(p) $MgCl_2$
B. Albite	(q) MgO
C. A salt of carnalite	(r) $NaAlSi_3O_8$
D. Glauber's salt	(s) $Na_2SO_4.10H_2O$

172. Match the following:

Column I	Column II
A. Efflorescent	(p) NaOH
B. Deliquescent	(q) KOH
C. Fusion mixture	(r) Na_2CO_3 and K_2CO_3
D. Washing soda	(s) $Na_2CO_3.10H_2O$

173. Match the following:

Column I	Column II
A. Beryl	(p) $KCl.MgCl_2.6H_2O$
B. Carnalite	(q) $MgCO_3$
C. Asbestos	(r) $3BeO.Al_2O_3.6SiO_2$
D. Magnesite	(s) $Ca_2Mg_5Si_8O_{22}(OH)_2$

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Matrix–Match Type Questions

171. (a)-(q), (b)-(r), (c)-(p), (d)-(s)

172. (a)-(q), (b)-(p), (c)-(r), (d)-(s)

173. (a)-(r), (b)-(p), (c)-(s), (d)-(q)

174. (a)-(q), (b)-(r), (c)-(p), (d)-(s)

175. (a)-(s), (b)-(r), (c)-(q), (d)-(p)

176. (a)-(q), (r), (b)-(q), (r), (c)-(q), (s), (d)-(p), (q)

177. (a)-(q), (b)-(r), (c)-(s), (d)-(p)

178. (a)-(s), (b)-(q), (c)-(r), (d)-(p)

179. (a)-(q), (b)-(p), (c-) (s), (d)-(r)

180. (a)-(s), (b)-(q), (r), (c)-(r), (d)-(p)

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181. (c) 182. (a) 183. (b) 184. (c)

185. (a) 186. (b) 187. (a,b)

HINTS AND EXPLANATIONS

Straight Objective Type Questions

1. Glauber's salt is $Na_2SO_4.10H_2O$.

2. $MgCO_3$ and $CaCO_3$ are water insoluble. $CaSO_4$ dissolves in water adding Ca^{2+} ions which are responsible for producing hardness in water.

3. Due to efflorescence (to give out H_2O) nature of $Na_2CO_3.10H_2O$.

4. Fluorspar is CaF_2. It does not contain aluminium. Feldspar is $KAlSi_3O_8$.

5. Calcium is obtained by electrolysis of a used mass consisting 6 parts $CaCl_2$ and 1 part CaF_2 at about 700°C in an electrolytic cell made of graphite which acts as anode and a water cooled cathode of iron.

$CaCl_2 \rightleftharpoons Ca^{2+} + 2Cl^-$

At anode: $2Cl^- \longrightarrow Cl_2 + 2e^-$

At cathode: $Ca^{2+} + 2e \longrightarrow Ca$

6. $AlCl_3$ exists as a dimmer (Al_2Cl_6). It is a strong Lewis acid as Al has an incomplete octet and has a tendency to gain electrons. $AlCl_3$ undergoes hydrolysis easily and forms an acidic solution.

$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$

Example, $AlCl_3$ sublimes at 100°C under vaccum.

9. Be and Mg atoms are smaller. The electrons in these atoms, are more strongly bound and hence these are not excited by the energy of flame to higher energy states. The chlorides of these elements therefore, do not give any colour in flame.

10. $4KO_2 + 2CO_2 \longrightarrow 2K_2CO_3 + 3O_2$

11. $2NaOH + CO_2 \longrightarrow \underset{\text{(Solid)}}{Na_2CO_3}$

12. $Na_2O_2 + \underset{\text{(20\% ice cold)}}{H_2SO_4} \longrightarrow Na_2SO_4 + H_2O_2$

13. $KHC_4H_4O_6$ is potassium hydrogen tartarate and is used to transform baking soda into baking powder.

17. The free ammoniated electrons make the solution of Na in liquid NH_3 a very powerful reducing agent. The ammonical solution of an alkali metal is rather favoured as a reducing agent than its aqueous solution because in aqueous solution, the alkali metal being highly electropositive evolves hydrogen from water (thus H_2O acts as an oxidizing agent) while its solution in ammonia is quite stable, provided no catalyst (transition metal) is present.

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Comprehension–5

145. $3Ca + N_2 \longrightarrow Ca_3N_2$
(A) (B), Calcium nitride (An ionic compound)

$Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2NH_3$
(C) Calcium hydroxide (D)

146. As calcium can form complexes only with strong complexing agents like EDTA.

Comprehension–6

147. (X) is $NaHCO_3$ (molecular wt. = 84)

148. $2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3(s) + CO_2(g) + H_2O(g)$
(X) (Y) (A) (B)

2 x 84 = 168g	106 g	44 g	18 g
≈ 16.8 g	10.6 g	4.4 g	1.8 g

$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$
Lime water — White ppt.

H_2O (g) is condensed to liquid water.

149. $Na_2CO_3 + BaCl_2 \longrightarrow BaCO_3 + NaCl$
(Y) (Z)

$BaCO_3 + 2HCl \longrightarrow BaCl_2 + H_2O + CO_2$
(Z)

Assertion and Reasoning Questions

150. Sodium metal can be obtained by electrolysis of fused salt.

153. As the size of the ion increases, the tendency to rupture the O–H bond decreases and hence acidic nature decreases i.e., basic nature increases.

154. Hydration energy decreases down the group i.e., Li is most hydrated the least conducted in aqueous solution.

155. Al metal is rendered passive when treated with conc. HNO_3.

163. K^+ being larger in size than Na^+ has a weaker positive field around it which cannot prevent the conversion of peroxide ion (O_2^{2-}) to superoxide ion $(O)_2^-$.

165. As it is a basic flux hence removes acidic impurities.

167. $BeCl_2 + 2H_2O \longrightarrow Be(OH)_2 + 2HCl$

169. NaCl and $CaCl_2$ are added to provide conductivity to the electrolyte and also to lower the fusion temperature of anhydrous $MgCl_2$.

170. Blue colour is due to solvated electrons.

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181. $CsBr_3$ contains Cs^+ and Br_3^- ($Br^- + Br_2$) ions.

182. Highly pure dilute solution of sodium in liquid ammonia is blue in colour due to ammoniated electron. This solution is conducting due to both ammoniated cation and ammoniated electron.

$Na + (x + y) NH_3 \longrightarrow [Na(NH_3)x]^+ + [e (NH_3)y]^-$

183. $2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$

184. Polyphosphates are used as water softener because these form soluble complexes with cationic species (Ca^{+2} and Mg^{+2}) present in hard water. The complex calcium and magnesium ions do not form any precipitate with soap and hence water readily produce lather with soap solution.

$2Ca^{+2} + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6] + 4Na^+$

$2Mg^{+2} + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Mg_2(PO_3)_6]$
$Na_2[Mg_2(PO_3)_6] + 4Na^+$
Soluble complex

185. Test of Mg^{2+} ion

$Mg^{2+} + NH_4OH + Na_2HPO_4 \longrightarrow Mg(NH_4)PO_4$

186. It is a case of disproportion reaction in which white phosphorus on reaction with NaOH gives PH_3 and sodium hydrogen phosphite as follows:

$P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$

187. Here Both Na_2O and Na_2O_2 are formed.

$2Na \xrightarrow[O_2]{Air} Na_2O \xrightarrow{O_2} Na_2O_2$

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25. Write balanced equation for the reactions between (a) Na_2O_2 and water (b) KO_2 and water (c) Na_2O and CO_2

26. An unknown solid mixture contains one or two of the following: $CaCO_3$, $BaCl_2$, $AgNO_3$, Na_2SO_4, $ZnSO_4$ and NaOH. The mixture is completely soluble in water and the solution gives pink colour with phenolphthalein. When dilute hydrochloric acid is gradually added to this solution, a precipitate is produced which dissolves with further addition of the acid. What is present in solid mixture? Give equations to explain the appearance of the precipitate and its dissolution.

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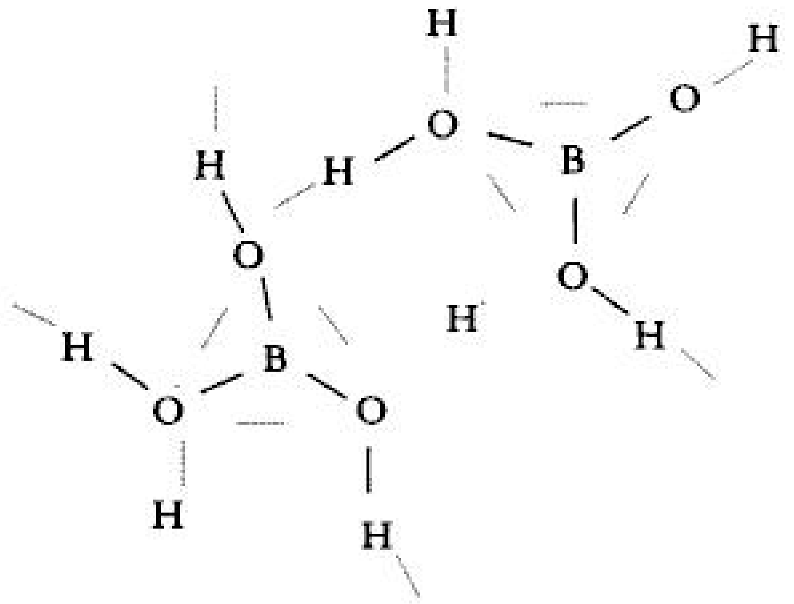

Fig. 5.4 St. of Boric acid

Uses

1. It is used as a antiseptic and a eye lotion (boric lotion).
2. It is also used as a food preservative.
3. H_3BO_3 decreases thermal expansion of glass.
4. It is used in the manufacture of enamels and glazes for pottery.

Borax or Tincal ($Na_2B_4O_7.10H_2O$)

It is called sodium tetraborate decahydrate.

It is also called tincal or suhaga as tincal has nearly 45% borax.

Preparation

1. **From Colemanite**: It is prepared from powdered ore of colemanite [$Ca_2B_6O_{11}$] by boiling it with sodium carbonate followed by filtration as follows:

$$Ca_2B_6O_{11} + 2Na_2CO_3 \longrightarrow Na_2B_4O_7 + 2NaBO_2 + 2CaCO_3$$

Sodium metaborate can be further converted into borax by passing CO_2 through it.

$$4NaBO_2 + CO_2 \longrightarrow Na_2B_4O_7 + Na_2CO_3$$

2. **From Boric Acid**: Boric acid on treatment with sodium carbonate gives borax as follows:

$$4H_3BO_3 + Na_2CO_3 \longrightarrow Na_2B_4O_7 + 6H_2O + CO_2$$

Physiochemical Properties

1. It exists in three forms:

(i) ***Prismatic Borax*** i.e., decahydrate form ($Na_2B_4O_7.10H_2O$): It can be obtained by the crystallization of borax solution at coordinate temperature. It is less soluble in cold water but highly soluble in hot water.

(ii) ***Octahedral Borax*** i.e., pentahydrate form ($Na_2B_4O_7.5H_2O$): It can be obtained by crystallizing borax solution at 333K.

(iii) ***Anhydrous Borax or Borax Glass*** ($Na_2B_4O_7$): It can be obtained heating borax above its melting point (1013K). This type of borax is colourless galassy mass which absorbs moisture and readily changes into decahydrate form.

2. **Hydrolysis**: On hydrolysis it gives basic taqueous solution as follows:

$$Na_2B_4O_7 + 7H_2O \xrightarrow{\Delta} 2Na^+ + 2\,OH^- + 4H_3BO_3$$

3. **Heating Effect of Borax**: Borax on heating swells up as water molecules are eliminated. When it is further heated at a high temperature a glassy transparent solid mass is obtained.

$$\underset{\text{Prismatic Borax}}{Na_2B_4O_7.10H_2O} \xrightarrow[-10H_2O]{\Delta} \underset{\text{Anhydrous borax}}{Na_2B_4O_7}$$

$$Na_2B_4O_7 \xrightarrow[740^\circ C]{\Delta} 2\underset{\text{Sodium metaborate}}{NaBO_2} + \underset{\text{(Glassy mass)}}{B_2O_3}$$

4. B_2O_3 (acidic, glass like) is used in borax bead test for detecting the presence of basic radicals like

[Co^{+3}, Cu^{+2}, Cr^{+2}, Ni^{+2}, Fe^{+2}]
(Co^{+3}, Cu^{+2}: Blue; Cr^{+2}: Green; Ni^{+2}: brown; Fe^{+2}: yellow)

$$B_2O_3 + \text{Pt-wire} + \text{Metal peroxide} \longrightarrow \underset{\text{Coloured Bead}}{\text{Metaborates}}$$

$$CuSO_4 + B_2O_3 \longrightarrow \underset{\text{Copper metaborate}}{CuO.B_2O_3} + SO_3$$

5. **With Ethyl Alcohol and conc. H_2SO_4**: When it is heated with ethyl alcohol and conc. H_2SO_4 volatile vapours of triethyl borate are produced which burn with a green edged flame (test of borate ions).

3. **Acidic Nature**: It is an acidic oxide as it forms carbonic acid on dissolving in water and can form salts with bases as follows:

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$$

4. **Action on Lime Water**: CO_2 turns limewater into milky in soluble calcium carbonate.

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{Milky}}{CaCO_3\downarrow} + H_2O$$

This milkiness disappears when more CO_2 is passed as soluble calcium bicarbonate is formed.

$$CaCO_3 + H_2O + CO_2 \longrightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2}$$

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + CO_2 + H_2O$$

5. **Formation of Carbonates**: It reacts with some basic oxides like Na_2O, K_2O to form their carbonates.

$$K_2O + CO_2 \longrightarrow K_2CO_3$$

$$Na_2O + CO_2 \longrightarrow Na_2CO_3$$

6. **Photosynthesis**: Here, CO_2 is changed into carbohydrates (glucose) etc. by plants in presence of sunlight and chlorophyll

$$6CO_2 + 6H_2O \xrightarrow[\text{Sun light}]{\text{Chlorophyll}} C_6H_{12}O_6 + 6O_2$$

$$6xCO_2 + 5xH_2O \longrightarrow (C_6H_{10}O_5)x + 6xO_2$$

Uses

1. It is used in cold drinks and aerated water.
2. CO_2 (15%) is used as fire extinguisher (except Mg-fire).
3. O_2 + 5–10% CO_2 is carbogen which is used for artificial respiration in case of CO poisoning and pneumonia patients.
4. It is used in the manufacture of sodium carbonate by solvay method.
5. Dry fire extinguisher is $SiO_2 + NaHCO_3$.
6. Foamite fire extinguisher is $NaHCO_3 + Al_2(SO_4)_3$.

Structure

It is a linear molecule with zero dipole moment. Here C–O bond length is 1.15 Å (less than C=O bond) as it is resonance hybrid of following structures.

$$O{=}C{=}O \longleftrightarrow \overset{+}{O}{\equiv}C{-}\overset{-}{O} \longleftrightarrow \overset{-}{O}{-}C{\equiv}\overset{+}{O}$$

- Carbon can also form some other oxides like C_3O_2, C_5O_2 etc., which are less stable. Some graphite oxides like C_2O and C_2O_3 are also formed which are very unstable.

Carbon Suboxide (C_3O_2) (O=C=C=C=O)

It is obtained by the dehydration of malonic acid.

$$CH_2\begin{cases}COOH\\COOH\end{cases} \xrightarrow{\Delta,\ P_4O_{10}} O{=}C{=}C{=}C{=}O + 2H_2O$$

Some of the chemical reactions of C_3O_2 are as follows:

$$C_3O_2 + 2H_2O \longrightarrow \underset{\text{Malonic acid}}{CH_2\begin{cases}COOH\\COOH\end{cases}}$$

$$C_3O_2 + 2HCl \longrightarrow \underset{\text{Malonyl chloride}}{CH_2\begin{cases}COCl\\COCl\end{cases}}$$

$$C_3O_2 + 2NH_3 \longrightarrow \underset{\text{Malonyl amide}}{CH_2\begin{cases}CONH_2\\CONH_2\end{cases}}$$

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$$2NH_4OH \xrightarrow{HgCl_2} Hg(NH_2)Cl + H_2O + NH_4Cl$$

Mercuric aminochloride (White ppt.)

$$2NH_4OH \xrightarrow{Hg_2Cl_2} Hg + Hg(NH_2)Cl + NH_4Cl + H_2O$$

Mercury mercuric amino chloride (Black ppt.)

$$4NH_4OH \xrightarrow{CuSO_4} Cu(NH_3)_4SO_4 + 4H_2O$$

Tetraamine copper sulphate (Deep blue colour)

$$4NH_4OH \xrightarrow{ZnCl_2} Zn(NH_3)_4Cl_2 + 4H_2O$$

$$4NH_4OH \xrightarrow{ZnSO_4} Zn(NH_3)_4SO_4 + 4H_2O$$

Tetraamine zinc sulphate (water soluble compound)

11. **With Nesseler's Reagent**: Here a red brown precipitate of millon's base of iodide is formed when ammonia is treated with alkaline solution of K_2HgI_4 (Nesseler's reagent) as follows:

$$2K_2HgI_4 + NH_3 + 3KOH \longrightarrow H_2N.HgO.HgI\downarrow + 7KI + 2H_2O$$

Brown ppt.

Uses

1. It is used in the preparation of nitric acid and other nitrogen compounds.
2. It is widely used in the preparation of nitrogenous fertilizers e.g., urea, ammonium nitrate, ammonium phosphate, ammonium sulphate etc.
3. It is used for making artificial silk and as a cleansing agent for removing grease in dry cleaning.
4. It is used in the preparation of sodium bicarbonate by Solvay's process.
5. Liquid ammonia is used as a refrigerant in ice plants.

Nitrous Acid (HNO_2)

Preparation

1. **From Barium Nitrate**: By adding calculated amount of ice, cold sulphuric acid to a well cooled solution of barium nitrate solution, nitrous acid is formed as follows:

$$Ba(NO_2)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HNO_2$$

2. **By the action of mineral acids on nitrites:**

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$

$$2KNO_2 + H_2SO_4 \longrightarrow K_2SO_4 + 2HNO_2$$

3. **By the oxidation of ammonia with H_2O_2:**

$$NH_3 + 2H_2O_2 \longrightarrow HNO_2 + 4H_2O$$

Physiochemical Properties

1. It has a slightly bluish colour in solution which is believed to be due to the anhydride N_2O_3.
2. It is a weak acid ($Ka = 4.5 \times 10^{-5}$) and reacts with alkalies to form salts.

$$NaOH + HNO_2 \longrightarrow NaNO_2 + H_2O$$

3. **Decomposition**: It is very unstable and undergoes autooxidation even on standing. On boiling it decomposes rapidly giving acid.

$$3HNO_2 \xrightarrow{Boil} HNO_3 + H_2O + 2NO$$

Brown fumes

4. **Oxidizing Property**: It acts as an oxidizing agent.

$$H_2S + 2HNO_2 \longrightarrow S + 2NO + 2H_2O$$

$$SO_2 + 2HNO_2 \longrightarrow H_2SO_4 + 2NO$$

$$KI + 2HNO_2 \longrightarrow 2KOH + 2NO + I_2$$

$$2FeSO_4 + H_2SO_4 + 2HNO_2 \longrightarrow Fe_2(SO_4)_3 + 2NO + 2H_2O$$

$$SnCl_2 + 2HCl + 2HNO_2 \longrightarrow SnCl_4 + 2NO + 2H_2$$

5. **Reducing Property**: It acts as a reducing agent towards strong oxidizing agent.

$$2KMnO_4 + 3H_2SO_4 + 5HNO_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5HNO_3$$

$$K_2Cr_2O_7 + 4H_2SO_4 + 3HNO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3HNO_3$$

$$Br_2 + H_2O + HNO_2 \longrightarrow HNO_3 + 2HBr$$

6. **With Ammonia**: It reacts with ammonia gives nitrogen and water.

$$NH_3 + HNO_2 \longrightarrow [NH_4NO_2] \longrightarrow N_2 + 2H_2O$$

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(iii) *In Case of Tin*

Dilute nitric acid and tin give tin nitrate and ammonium nitrate

$$\underset{\text{(dil.)}}{4Sn + 10HNO_3} \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

Hot and concentrated nitric acid and tin give meta stannic acid and nitrogen dioxide.

$$\underset{\text{(hot and conc.)}}{Sn + 4HNO_3} \longrightarrow \underset{\text{Metastannic acid}}{H_2SnO_3} + 4NO_2 + H_2O$$

(iv) *In Case of Lead*

Dilute nitric acid and lead give lead nitrate and nitric oxide.

$$\underset{\text{(dil.)}}{3Pb + 8HNO_3} \longrightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

Concentrated nitric acid and lead give lead nitrate and nitrogen dioxide.

$$\underset{\text{(conc.)}}{Pb + 4HNO_3} \longrightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O$$

- **Oxidation of Metals below Hydrogen in Electrochemical Series**: As these metals are not only less electropositive but also less reactive than hydrogen hence cannot displace nascent hydrogen from nitric acid. Such metals can be oxidize into their oxides by nitric acid. These oxides dissolve in nitric acid to form nitrates as follows:

$$HNO_3 \longrightarrow \text{Reduction product} + H_2O + [O]$$

$$\text{Metal} + [O] \longrightarrow \text{Metal oxide}$$

$$\text{Metal oxide} + HNO_3 \longrightarrow \text{Metal nitrate} + H_2O$$

(i) *In Case of Copper*

Cold and very dilute nitric acid and copper give copper nitrate and nitrous oxide.

$$\underset{\text{(cold and dil.)}}{4Cu + 10HNO_3} \longrightarrow 4Cu(NO_3)_2 + 5H_2O + N_2O$$

Cold and dilute nitric acid and copper give copper nitrate and nitric oxide.

$$\underset{\text{(cold and moderately conc.)}}{3Cu + 8HNO_3} \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$$

Hot and concentrated nitric acid and copper give copper nitrate and nitrogen dioxide.

$$\underset{\text{(hot and conc.)}}{Cu + 4HNO_3} \longrightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$$

$$\underset{\text{(cold and dil.)}}{5Cu + 12HNO_3} \longrightarrow 5Cu(NO_3)_2 + 6H_2O + N_2$$

(ii) *In Case of Silver*

Dilute nitric acid and silver give silver nitrate and nitric oxide.

$$\underset{\text{(dil.)}}{3Ag + 4HNO_3} \longrightarrow 3AgNO_3 + NO + 2H_2O$$

Concentrated nitric acid and silver give silver nitrate and nitrogen dioxide.

$$\underset{\text{(conc.)}}{Ag + 2HNO_3} \longrightarrow AgNO_3 + NO_2 + H_2O$$

In Case of Mercury

Dilute nitric acid and mercury give mercurous nitrate and nitric oxide.

$$\underset{\text{(dil.)}}{6Hg + 8HNO_3} \longrightarrow \underset{\text{Mercurous nitrate}}{3Hg_2(NO_3)_2} + 2NO + 4H_2O$$

Concentrated nitric acid and mercury give mercuric nitrate and nitrogen dioxide.

$$\underset{\text{(conc.)}}{Hg + 4HNO_3} \longrightarrow \underset{\text{Mercuric nitrate}}{Hg(NO_3)_2} + 2NO_2 + 2H_2O$$

- **In case of Noble Metals**: Nobles metals like Au, Pt, Rh, Ir etc., are not effected by nitric acid but in aqua regia these metals dissolve as follows:

  Gold dissolves in aqua regia to give chloro auric acid and nitrosyl chloride as follows:

$$2Au + 3HNO_3 + 11HCl \longrightarrow \underset{\substack{\text{Chloro auric acid}\\\text{(Hydrogen tetrachloro aurate)}}}{2HAuCl_4} + 3NOCl + 6H_2O$$

  Platinum dissolves in aqua regia to give chloro platinic acid and nitrosyl chloride as follows:

$$Pt + 2HNO_3 + 8HCl \longrightarrow \underset{\text{Chloroplatinic acid}}{H_2PtCl_6} + 2NOCl + 4H_2O$$

- **In Case of Mg and Mn**: Both these metals on reaction with dilute nitric acid form their nitrates and liberate hydrogen as follows:

$$\underset{\text{(dil.)}}{Mg + 2HNO_3} \longrightarrow Mg(NO_3)_2 + H_2\uparrow$$

$$\underset{\text{(dil.)}}{Mn + 2HNO_3} \longrightarrow Mn(NO_3)_2 + H_2\uparrow$$

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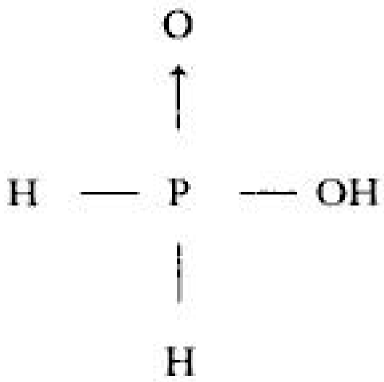


Phosphorous Acid (H_3PO_3)

Preparation

1. It is prepared by the action of water upon phosphorous oxide, or by the action of water on phosphorous trichloride.

$$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$$

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

2. It can be prepared by the hydrolysis of PCl_3 by oxalic acid.

$$PCl_3 + 3H_2C_2O_4 \longrightarrow H_3PO_3 + 3CO + 3CO_2 + 3HCl$$

Physiochemical Properties

1. It is a white deliquescent crystal with a melting point of 73.6°C and highly soluble in water.
2. It is a dibasic acid which ionizes as follows:

$$H_3PO_3 \longrightarrow H_2PO_3^- + H^+$$

$$H_2PO_3^- \longrightarrow HPO_3^{2-} + H^+$$

As it is a weak dibasic acid hence it forms two series of salts, e.g, sodium dihydrogen phosphite NaH_2PO_3 and disodium hydrogen phosphite, Na_2HPO_3.

3. **Decomposition**: It decomposes on heating at 200°C into phosphoric acid and phosphine.

$$4H_3PO_3 \longrightarrow \underset{\text{Orthophosphoric acid}}{3H_3PO_4} + PH_3$$

4. **Reducing Nature**: It can act as a strong reducing agent For example:

- It reduces silver nitrate to metallic silver.

$$2AgNO_3 + H_3PO_3 + H_2O \longrightarrow 2Ag\downarrow + 2HNO_3 + H_3PO_4$$

- It reacts with $HgCl_2$ to form a white precipitate of Hg_2Cl_2 which subsequently turns black due to separation of metallic mercury.

$$2HgCl_2 + H_3PO_3 + H_2O \longrightarrow Hg_2Cl_2\downarrow + 2HCl + H_3PO_4$$

$$Hg_2Cl_2 + H_3PO_3 + H_2O \longrightarrow 2Hg\downarrow + 2HCl + H_3PO_4$$

- It reduces copper sulphate into copper.

$$H_3PO_3 + CuSO_4 + H_2O \longrightarrow H_3PO_4 + H_2SO_4 + Cu\downarrow$$

- It reduces auric chloride into gold.

$$3H_3PO_3 + 2AuCl_3 + 3H_2O \longrightarrow 3H_3PO_4 + 6HCl + 2Au\downarrow$$

- It reduces sulphur dioxide into sulphur.

$$SO_2 + 2H_3PO_3 \longrightarrow 2H_3PO_4 + S\downarrow$$

- It reduces PCl_5 into PCl_3.

$$H_3PO_3 + 3PCl_5 \longrightarrow PCl_3 + 3POCl_3 + 3HCl$$

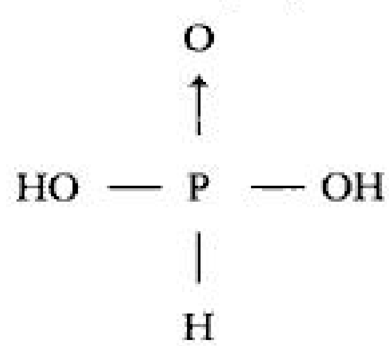
- It decolourizes the solution of iodine and potassisum permanganate by reducing them as follows:

$$I_2 + H_2O + H_3PO_3 \longrightarrow H_3PO_4 + 2HI$$

$$2KMnO_4 + 3H_2SO_4 + 5H_3PO_3 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5H_3PO_4$$

Structure

Here, phosphorous atom is sp^3 hybridized.



Orthophosphoric Acid (H_3PO_4)

Preparation

1. It can be conveniently prepared by dissolving P_2O_5 in water and the solution is boiled to form thick syrup.

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4$$

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(a) 2, 2 (b) 1, 8
(c) 1, 2 (d) 1, 4

17. The equivalent mass of phosphoric acid (H_3PO_4) in the reaction,

$NaOH + H_3PO_4 \longrightarrow NaH_2PO_4 + H_2O$ is

(a) 98 (b) 89
(c) 49 (d) 58

18. Correct order of boiling points of hydrides of nitrogen family is

(a) $NH_3 < PH_3 < AsH_3 < SbH_3$

(b) $PH_3 < AsH_3 < NH_3 < SbH_3$

(c) $NH_3 < SbH_3 < PH_3 < AsH_3$

(d) $PH_3 < NH_3 < SbH_3 < AsH_3$

19. Ammonium compound which on heating does not give NH_3 is

(a) $(NH_4)_2SO_4$ (b) $(NH_4)_2CO_3$
(c) NH_4NO_2 (d) NH_4Cl

20. Which of the following oxides of nitrogen is a coloured gas?

(a) N_2O (b) NO
(c) N_2O_4 (d) NO_2

21. The number of P–O–P bridges in the structure of phosphorous pentoxide and phosphorous trioxide are, respectively

(a) 5, 5 (b) 5, 6
(c) 6, 5 (d) 6, 6

22. Addition of concentrated HNO_3 to concentrated H_2SO_4 gives

(a) SO_4^{2-} (b) SO_3
(c) NO_2^+ (d) NO_3^-

23. H_3PO_2 is the molecular formula of an acid of phosphorous. Its name and basicity are, respectively

(a) Hypophosphoric acid and two

(b) Hypophosphorous acid and one

(c) Hypophosphorous acid and two

(d) Phosphorous acid and two

24. The strongest base is

(a) NH_3 (b) PH_3
(c) AsH_3 (d) SbH_3

25. Ionization of boric acid in aqueous medium gives, which one of the following?

(a) $[BO_3]^{3-}$ (b) $[B(OH)_4]^-$
(c) $[B(OH)_2O]^-$ (d) $[B(OH)O_2]^{2-}$

26. Which of the following halide of carbon is used as refrigerant?

(a) CCl_4 (b) CF_4
(c) CH_2Cl_2 (d) CF_2Cl_2

27. In $[B_4O_5(OH)_4]^{2-}$ anion, what is the number of B–O–B bridges?

(a) 2 (b) 3
(c) 4 (d) 5

28. Which of these is most explosive?

(a) NCl_3 (b) PCl_3
(c) $AsCl_3$ (d) All of these

29. Two oxides of nitrogen, NO and NO_2 react together at 253°K and form a compound of nitrogen X. X reacts with water to yield another compound of nitrogen Y. The shape of the anion of Y molecule is

(a) triangular planar

(b) pyramidal

(c) tetrahedral

(d) square planar

30. Concentrated HNO_3 reacts with iodine to give:

(a) HI (b) HOI
(c) $HOIO_2$ (d) $HOIO_3$

31. The reaction between NH_2^- and N_2O gives

(a) NO (b) N_2O_5
(c) N_3^- (d) NH_2NH_2

32. The lightening bolts in the atmosphere cause the formation of

(a) NO (b) NH_3
(c) NH_4OH (d) NH_2OH

33. Which of the following statement is correct?

(a) NO is acidic colourless and gaseous oxide.

(b) N_2O is angular in shape.

(c) NO_2 is angular in shape with a sweet smell.

(d) NO_2 reacts with NaOH to give a mixture of two salts.

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(a) Both are triatomic and colourless.
(b) Both are triatomic and diamagnetic.
(c) Both are odourless.
(d) None of these.

75. For $P_4 + Cl_2$ (excess) $\longrightarrow$ (A) $\xrightarrow{H_2O}$ (B) + (C)
Any alkene can react with (C) to give a compound which can perform Wurtz reaction. Here (B) is
(a) HCl (b) H_3PO_2
(c) H_3PO_4 (d) H_3PO_3

76. Consider the following statements for diborane.
I Boron is approximately sp^3 hybridized.
II B–H–B angle is 180°.
III There are two terminal B–H bonds for each boron atom.
IV There are only 12 bonding electrons available.

(a) 1, 2 and 3 are correct
(b) 2, 3 and 4 are correct
(c) 1, 3 and 4 are correct
(d) 1, 2 and 4 are correct

77. The lightening bolts in the atmosphere cause the formation of
(a) NH_3 (b) NO
(c) NH_2OH (d) NH_4OH

78. The yellow colour of conc. HNO_3 can be removed by
(a) Passing NH_3.
(b) Passing air through warm acid.
(c) Adding Mg powder.
(d) Boiling the acid.

79. P_4O_6 is heated with water to give
(a) Orthophosphoric acid
(b) Orthophosphorous acid
(c) Hypophosphorous acid
(d) Hypophorphoric acid

80. A certain salt (X) gives the following tests:
On strongly heating it swells to give glassy material. When concentrated H_2SO_4 is added to a hot concentrated solution of (X), white crystals of a weak acid separate out. Identify (X)?
(a) $NaBO_2$ (b) $Na_2B_4O_7$
(c) $Na_2S_2O_3$ (d) $Ca_2B_6O_{11}$

81. Among the following substituted silanes the one which will give rise to cross-linked silicone polymer on hydrolysis is
(a) R_4Si (b) $RSiCl_3$
(c) R_2SiCl_2 (d) R_3SiCl

82. Phosphorous on reaction with conc. HNO_3 gives an acid (A) which can also be formed by the action of dil. H_2SO_4 on powdered phosphorite rock. The acid (A) is
(a) H_3PO_3 (b) H_3PO_4
(c) H_3PO_2 (d) HPO_3

Multiple Correct Answer Type Questions (More Than One Choice)

83. Nitrogen (I) oxide is produced by
(a) Thermal decomposition of ammonium nitrate.
(b) Disproportionation of N_2O_4.
(c) Thermal decomposition of ammonium nitrite.
(d) Interaction of hydroxyl amine and nitrous acid.

84. Which one of the following is/are the incorrect statement(s)?
(a) Boric acid is a protonic acid
(b) Beryllium exhibits coordination number of six.
(c) Chlorides of both beryllium and aluminium have bridged chloride structures in solid phase.
(d) $B_2H_6.2NH_3$ is known as Inorganic Benzene.

85. Select the correct statements about diborane
(a) H_b ....B....H_b bond angle is 122°.
(b) All hydrogens in B_2H_6 lie in the same plane.
(c) B_2H_6 has three centered bond.
(d) Each boron atom lies in sp^3 hybrid state.

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(b) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is more directional.

(c) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies sp^3 orbital and is less directional.

(d) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional.

119. White phosphorus on reaction with NaOH gives PH_3 as one of the products. This is a
(a) Dimerization reaction
(b) Disproportional reaction
(c) Condensation reaction
(d) Precipitation reaction

Assertion and Reasoning Questions

In the following question two statements (Assertion) A and Reason (R) are given. Mark
(a) If A and R both are correct and R is the correct explanation of A.
(b) If A and R both are correct but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true.

120. (A): CF_4 and NF_3 cannot be hydrolyzed.
(R): Carbon and nitrogen both do not have vacant d-orbital.

121. (A): AlF_3 is an ionic compound whereas BF_3 is covalent compound.
(R): BF_3 involves back π bonding.

122. (A): BF_3 is a weaker Lewis acid than BCl_3.
(R): The planar BF_3 molecule is stabilized to a greater extent than BCl_3 by B–X π-bonding.

123. (A): Liquid ammonia is used for refrigeration.
(R): It vapourizes quickly.

124. (A): In N_2O_4 as solvent, substance as NOCl which yields NO^+ ions are regarded as acids.
(R): In N_2O_4 as solvent substances as $NaNO_3$ which yield NO_3^- ions are regarded as bases.

125. (A): An orthophosphoric acid is added to the Zimmermann Rein hard reagent during dichrometric titration of ferrous salts.
(R): Orthophosphoric acid reduces the potential of the iron couple, thus aiding the oxidation of a ferrous salt.

126. (A): HNO_3 is stronger acid than HNO_2.
(R): In HNO_3 there are two nitrogen and oxygen bonds whereas in HNO_2 there is only one such bond.

127. (A): A small piece of Zn metal dissolves in dilute HNO_3 but no is hydrogen evolved.
(R): HNO_3 is oxidizing acid and this oxidizes the evolved H_2 into water.

128. (A): Silicones are hydrophobic in nature.
(R): Si–O–Si linkages are moisture sensitive.

129. (A): On cooling, the brown colour of nitrogen dioxide disappears.
(B): On cooling, NO_2 undergoes dimerization resulting in the pairing of the odd electron in NO_2.

130. (a): Both H_3PO_4 and H_3PO_3 possess the same number of hydrogen atoms, yet H_3PO_4 behaves as a tribasic acid while H_3PO_3 behave as a dibasic acid.
(R): In H_3PO_4 there are three hydrogen atoms linked to phosphorous through oxygen atoms whereas in H_3PO_3 there are only two such hydrogen atoms.

131. (A): PF_5 and IF_5 have similar shapes.
(R): PF_5 has two types of P–F bond lengths.

132. (A): Boric acid behaves as a weak monobasic acid.
(R): Boric acid contains hydrogen bonds in its structure.

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32. $N_2 + O_2 \xrightarrow{\text{Lightening spark}} 2NO$

36. $Mg_3N_2(s) + 6H_2O(l) \longrightarrow 3Mg(OH)_2 + 2NH_3(g)$
1 mol 2 mol

38. Nitrogen has no d-orbitals in its valence shell.

39. SO_2 is highly soluble in water and therefore cannot be collected over water.

40. NO is the most thermally stable oxide of nitrogen.

$$2NO \xrightarrow{900°C} N_2 + O_2$$

$$2N_2O \xrightarrow{500–900°C} 2N_2 + O_2$$

$$N_2O_3 \xrightarrow{\text{room temperature}} NO + O_2$$

$$2N_2O_5 \xrightarrow{40°C} 4NO_2 + O_2$$

41. All alkali metal nitrates (except $LiNO_3$) on heating does not give NO_2 gas.

$$2KNO_3 \xrightarrow{\Delta} 2KNO_2 + O_2$$

43. Graphite show moderate conductivity due to the presence of unpaired or free fourth valence electron on each carbon atom.

49. $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$

50. $PH_4I + NaOH \longrightarrow NaI + PH_3 + H_2O$

Brainteasers Objective Type Questions

55. $HNO_2 + 2H_2SO_3 + H_2O \longrightarrow 2H_2SO_4 + NH_2OH$

59. $\underset{(A)}{CO} + NaOH \xrightarrow{\text{High, P\&T}} \underset{(B)}{HCOONa}$

$$\underset{(B)}{HCOONa} \xrightarrow{\Delta} \underset{(C)}{(COONa)_2} + H_2$$

$$(COONa)_2 + CaCl_2 \longrightarrow \underset{(D)}{CaC_2O_4} + 2NaCl$$

$$5CaC_2O_4 + 2KMnO_4 + 5H_2SO_4 \longrightarrow 5CaSO_4 + K_2SO_4 + MnSO_4 + 8H_2O + 10CO_2$$

63. $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

$$\underset{\text{Sodium azide}}{2NaN_3} \xrightarrow{\Delta} 2Na + 3N_2$$

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$$

69. Due to greater electronegativity (4.0), F pulls the lone pair of electrons on N towards itself resulting in the decrease in basic character.
The basic character in the increasing order is
$NF_3 < NCl_3 < NBr_3 < NI_3$

73. HI and HBr (in that order) are the strongest reducing hydracids and hence they reduce H_2SO_4. HCl is quite stable and hence is oxidized by strong oxidizing agent like $KMnO_4$. HF is not a reducing agent. In the smallest F^- ion, the electron which is to be removed during oxidation is closest to the nucleus and therefore most difficult to be removed. Therefore, HF is a poor reducing agent.

75. $2P + 5Cl_2 \longrightarrow \underset{(A)}{2PCl_5}$

$$2PCl_5 + 8H_2O \longrightarrow \underset{(B)}{2H_3PO_4} + \underset{(C)}{10HCl}$$

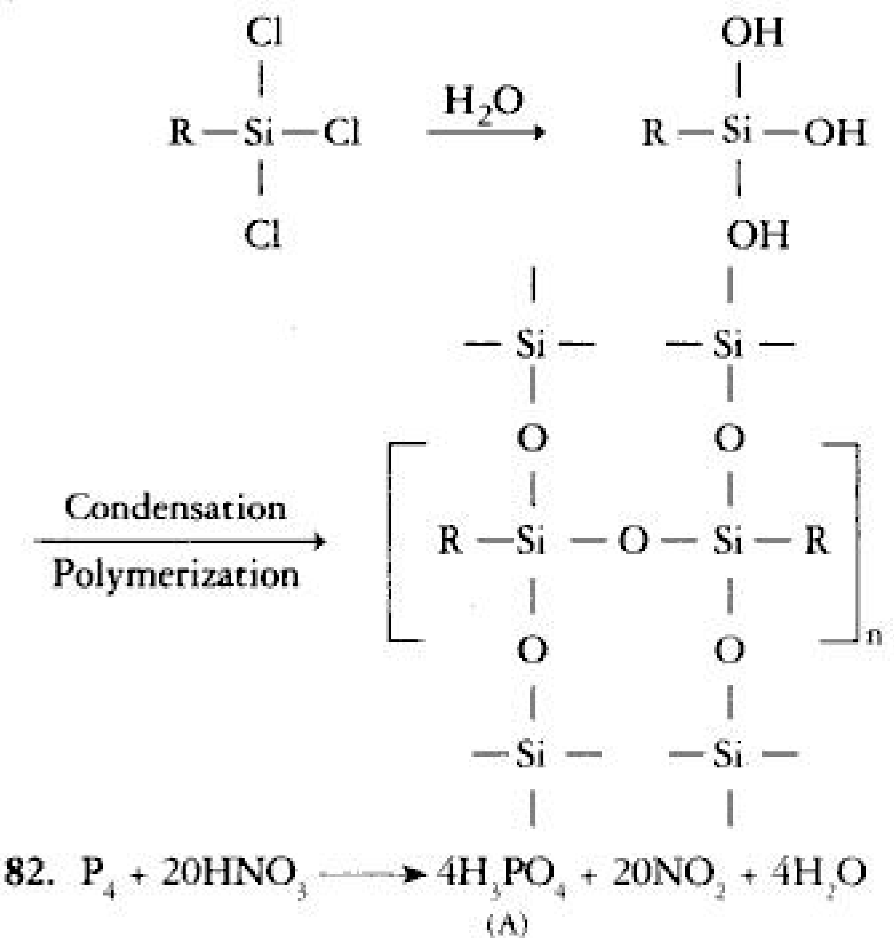
80. On strong heating it swells up to give a glassy mass so it may be borax. It is further confirmed as with H_2SO_4 it gives white crystals of boric acid (weak acid).

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 + 10H_2O$$

$$Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + \underset{\text{Glassy mass}}{B_2O_3}$$

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + \underset{\text{Weak acid}}{4H_3BO_3}$$

81.



82. $P_4 + 20HNO_3 \longrightarrow \underset{(A)}{4H_3PO_4} + 20NO_2 + 4H_2O$

$$P_4 + 10H_2SO_4 \longrightarrow \underset{\substack{\text{Phosphoric acid}\\(A)}}{4H_3PO_4} + 10SO_2 + 4H_2O$$

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THE PEARSON GUIDE TO

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Atul Singhal

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