CHEMICAL BONDING, COORDINATION CHEMISTRY & METALLURGY

CONTENTS

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COORDINATION CHEMISTRY

METALLURGY

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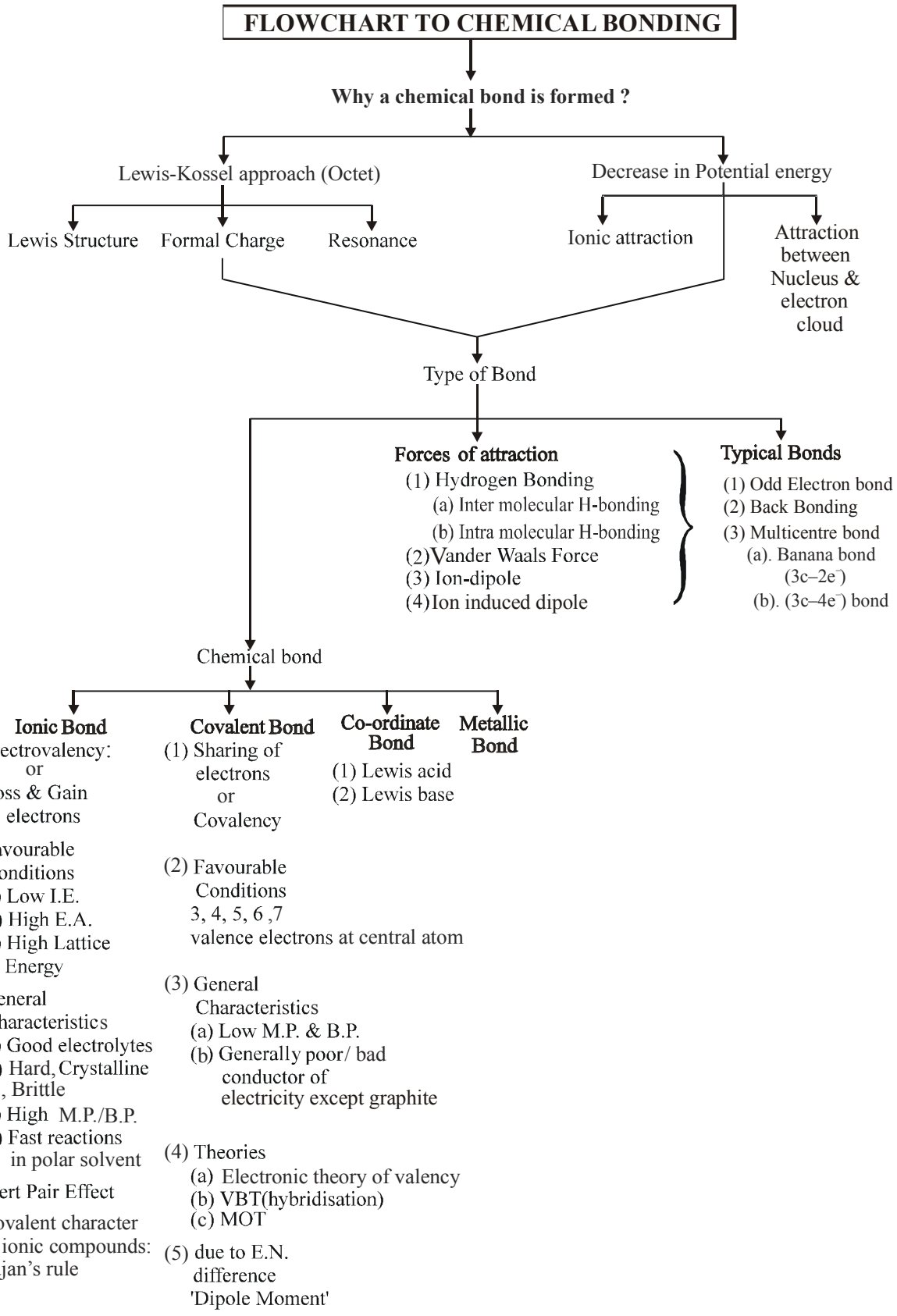
FLOWCHART TO CHEMICAL BONDING



Note : Hydrogen bond is an extreme manifestation of dipole dipole interaction.

VANDER WAAL'S FORCES

⇒ These are the weakest type of inter molecular forces that exist among the chemical species which being significant change in physical properties.

⇒ These are non-directional, non-valence cohesive forces. These attractive forces being played between the two molecules are independent of the presence of other molecules.

⇒ Solid, liquid or gaseous states of many molecules are explained on the basis of inter molecular forces other than covalent, ionic or metallic bonds. Although inert gases do not form any type of bond but may exist in liquid and solid states. This shows that the atoms of inert gases are attracted by each other through some type of inter molecular forces. These intermolecular forces are called Vander Waals forces.

Types of Vander Waal's Forces

(1) ***Dipole-dipole interaction (Keesom forces) :*** The force of attraction between the oppositely charged poles of two polar molecules (for example : H_2S, HCl, PH_3 etc.) is called dipole-dipole attraction.

(2) ***Dipole-induced dipole interaction (Debye forces) :*** This type of cohesive forces occurs in a mixture of polar and non polar molecules. The former induce polarity in non polar molecules by disturbing their electron system. for example force of attraction between Cl_2 and H_2O.

(3) ***Instantaneous dipole-Induced dipole interaction (Dispersion forces/London forces) :*** The weak intermolecular forces operating in similar non polar gaseous molecules are called London forces. These forces are very weak in nature and exists only at low temperature. For example weak intermolecular forces in F_2, Cl_2, N_2, molecules and in noble gasses.
(Note :- London forces present in both polar and non polar species)

Other Weak Interactions

(1) ***Ion-dipole interaction :*** Polar molecules are attracted by ions. The negative pole is attracted by cation and positive pole attracted by the anion. This type of attraction is called ion dipole attraction, ion-dipole attraction is observed generally in the process of solvation when sodium chloride (Na^+ Cl^-) is dissolved in water because negative poles of water aggregate around Na^+ ions and positive poles around Cl^- ions.

(2) ***Ion-induced dipole interaction :*** When non polar molecules come in contact with ions, its electron cloud gets polarised and the oppositely charged end of it is attracted by the ion. For example attraction between I^- and I_2 molecule.

HYBRIDISATION

The phenomenon of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. For example when one 2s and three 2p-orbitals of carbon hybridise, there is the formation of four new sp^3 hybrid orbitals.

Salient features of hybridisation: The main features of hybridisation are as under :

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are equivalent in energy and shape.
3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

Important conditions for hybridisation

(i) The orbitals present in the valence shell of the atom are hybridised.

(ii) The orbitals undergoing hybridisation should have almost equal energy.

(iii) Promotion of electron is not essential condition prior to hybridisation.

(iv) It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation.

Types of Hybridisation

There are various types of hybridisation involving s, p and d orbitals. The different types of hybridisation are as under :

(i) *sp hybridisation* (ii) sp^2 *hybridisation* (iii) sp^3 *hybridisation*

(iv) sp^3d *hybridisation:* (v) sp^3d^2 *hybridisation:* (vi) sp^3d^3 *hybridisation:*

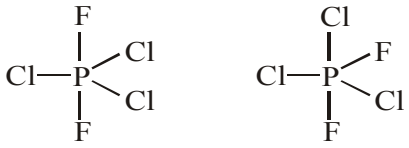
BENT'S RULE

(i) A lone pair of electron prefers to occupy that hybrid orbital which has greater percentage of s-character.

(ii) A more electronegative atom/group prefers to occupy that hybrid orbital which has smaller percentage of s-character.

Ex. Draw the geometry of PCl_3F_2

Sol.



Correct Structure

Wrong Structure

Because highly electronegative atom occupy axial position (axial position has smaller percentage of s-character).

DRAGO'S RULE

On the basis of experimental bond angles of certain molecules fulfilling the following three conditions,

(i) Central atom belongs to third or lower period in periodic table

(ii) Central atom must contain atleast one lone pair of electron

(iii) Electronegativity of surrounding atom is $\leqslant 2.5$

Drago generalised that in such molecules justification of experimental bond angle can be made satisfactory if one considers no hybridisation, i.e., overlapping of almost pure atomic orbitals from central atom.

In such molecules bond angle is approximately 90°.

Group 15	**Bond angle**	**Group 16**	**Bond angle**
NH_3	107°48'	H_2O	104°28'
PH_3	93°36'	H_2S	92°
AsH_3	91°48'	H_2Se	91°
SbH_3	91°18'	H_2Te	90.5°

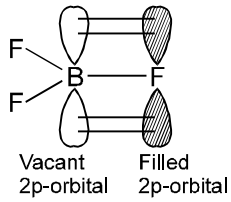
- Right order of bond angle.
  (a) $H_2O > H_2S > H_2Se > H_2Te$ (b) $NH_3 > PH_3 > AsH_3 > SbH_3$

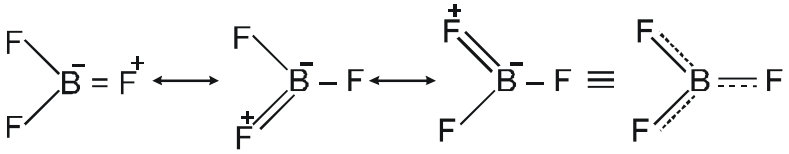
ELECTRON DEFICIENT BONDING

(a) Back Bonding

Back bonding generally takes place when out of two bonded atoms one of the atom has vacant orbitals(generally this atom is from second or third period) and the other bonded atom is having some non-bonded electron pair(generally this atom is from the second period). Back bonding increases the bond strength and decreases the bond length.

For example, in BF_3 the boron atom completes its octet by accepting 2p-electrons of fluorine into 2p empty orbital.





- Decrease in B – F bond length is due to delocalised pπ–pπ back bonding between filled p-orbital of F atom and vacant p-orbital of B atom.

The extent of back bonding is much larger if the orbitals involved in the back bonding are of same size, for example the extent of back bonding in boron trihalides is as follows :

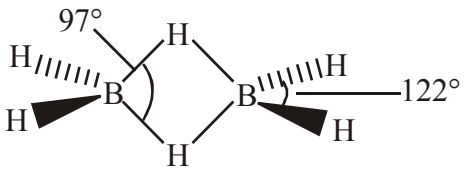
$BF_3 > BCl_3 > BBr_3$

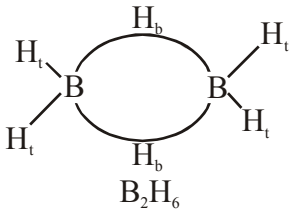
There is pπ-pπ back bonding in boron trihalide. The extent of back bonding decreases from BF_3 to BI_3 because of increasing size of p-orbitals participating in back bonding that is from 2p(in F) to 5p(in I).

(b) Bridge Bonding

There are many compounds in which some electron deficient bonds are present apart from normal covalent bonds or coordinate bonds which are 2c-2e$^-$ bonds(two centre two electron bonds). These electron deficient bonds have less number of electrons than the expected such as three centre-two electron bonds (3c-2e) which are present in diborane B_2H_6, $Al_2(CH_3)_6$, BeH_2(s) etc.

bonding in B_2H_6(diboarane)

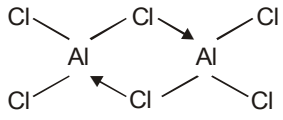




B_2H_6

The structure of diborane containing four terminal(t) and two bridging(b) hydrogen atoms. The model determined by molecular orbital theory indicates that the bonds between boron and the terminal hydrogen atoms are conventional 2c-2e$^-$ covalent bonds. The bonding between the boron atoms and the bridging hydrogen atoms is, however different from that in molecules such as hydrocarbons. Having used two electrons in bonding to the terminal hydrogen atoms, each boron has one valence electron remaining for additional bonding. The bridging hydrogen atoms provide one electron each. Thus the B_2H_2 ring is held together by four electrons, an example of 3c-2e$^-$bonding. This type of bond is sometimes called as **'banana bond'**. Group 13, gallium is known to form a similar compound, digallane, Ga_2H_6.

But Al_2Cl_6 have covalent bond only and there is no electron deficient bonding as depicted in the given structure.

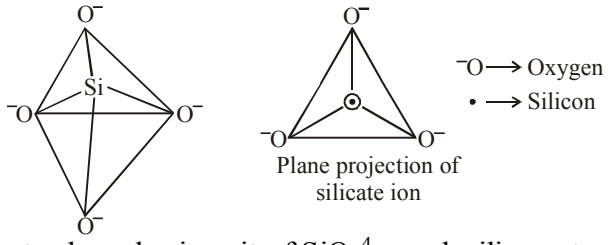


(Al – Cl – Al is 3c – 4e bond)

SILICATES

Silicates are metal derivatives of silicic acid, H_4SiO_4 or $Si(OH)_4$. Silicates are formed by heating metal oxide or metal carbonates with sand, e.g.,

$$Na_2CO_3 \xrightarrow[SiO_2]{\text{Fused with sand}} Na_4SiO_4,\ Na_2(SiO_3)_n,\ \text{etc.}$$



Silicates have basic unit of SiO_4^{4-}, each silicon atom is bonded with four oxide ions tetrahedrally. There are following types of silicates

Silicates	Sharing of O-atom / Basic Tetrahedral unit	Contribution of O-atom/Basic Tetrahedral unit	General formula
Ortho	0	4	SiO_4^{4-}
Pyro	1	3.5	$Si_2O_7^{-6}$
Cyclic	2	3	$(SiO_3)_n^{2n-}$ (n = finite)
Simple chain (pyroxene)	2	3	$(SiO_3)_n^{2n-}$ (n = infinite)
Double chain (Amphibole)	(3, 2) avg. = 2.5	$\frac{11}{4}=\left(\frac{5.5}{2}\right)$	$(Si_4O_{11})_n^{6n-}$
2D or (Sheet)	3	2.5	$(Si_2O_5)_n^{2n-}$
3D	4	2	$(SiO_2)_n$

INERT PAIR EFFECT

In p-block elements the stability of the lower oxidation state increases on descending the group. Because increased effective nuclear charge holds ns electrons tightly due to poor shielding effect of inner d & f orbitals and thereby, restrict their (ns electrons) participation in bonding only np electrons take part in bond formation. As a result of this, +1 oxidation state of Tl is more stable than it's +3 oxidation state. Pb shows +2 stable oxidation state and Bi shows +3 stable oxidation state.

For example :

Group 13	Group 14
B (+3)	C (+4)
Al (+3)	Si (+4)
Ga (+3), (+1)	Ge (+4), (+2)
In (+3), (+1)	Sn (+4), (+2)
Tl (+3), (+1)	Pb (+4), (+2)

Order of stability : $Tl^{+1} > In^{+1} > Ga^{+1}$ (due to inert pair effect)

Order of stability : $Pb^{+2} > Sn^{+2} > Ge^{+2}$ (due to inert pair effect)

Ex. $PbCl_4$ is stable at room temperature whereas PbI_4 doesn't exist.

Sol. Due to inert pair effect Pb(+4) is less stable than Pb(+2). Hence it is very good oxidant.

$Pb(IV) + 2e^- \longrightarrow Pb(II)$

Reducing abilities of halides follows the sequence

$I^- > Br^- > Cl^-$

MOLECULES THAT DO NOT EXIST

(1) SF_4, SF_6 & PF_5 exist while. OF_4, OF_6, NF_5 do not exist

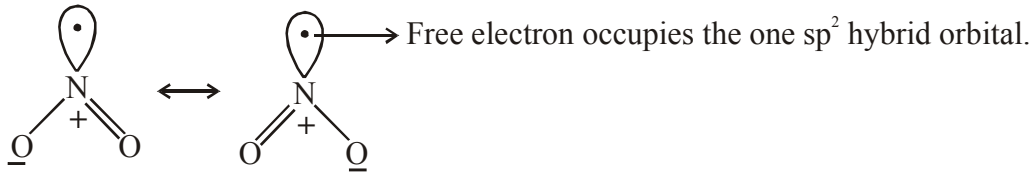
(2) (a) PI_5(vap) does not exist

(b) PI_5 (Solid) exist

(3) SF_6, PF_5, XeF_6, XeF_4 & XeF_2 exist while SH_6, PH_5, XeH_6, XeH_4, XeH_2 do not exist

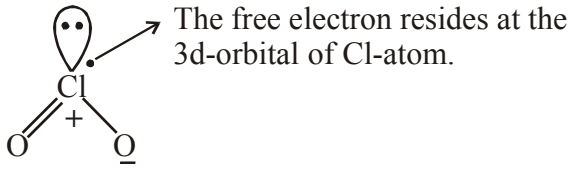
STRUCTURE OF ODD ELECTRONIC SPECIES

(1) NO_2



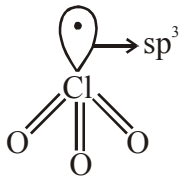
(2) ClO_2

Structure :-



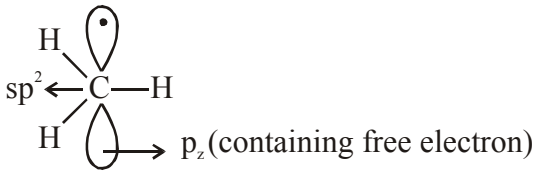
(3) ClO_3 :

Structure :



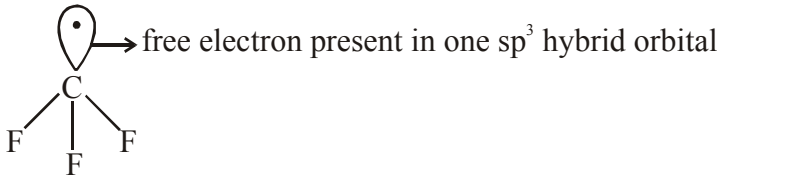
(4) $\dot{C}H_3$:

Structure :



(5) $\dot{C}F_3$:

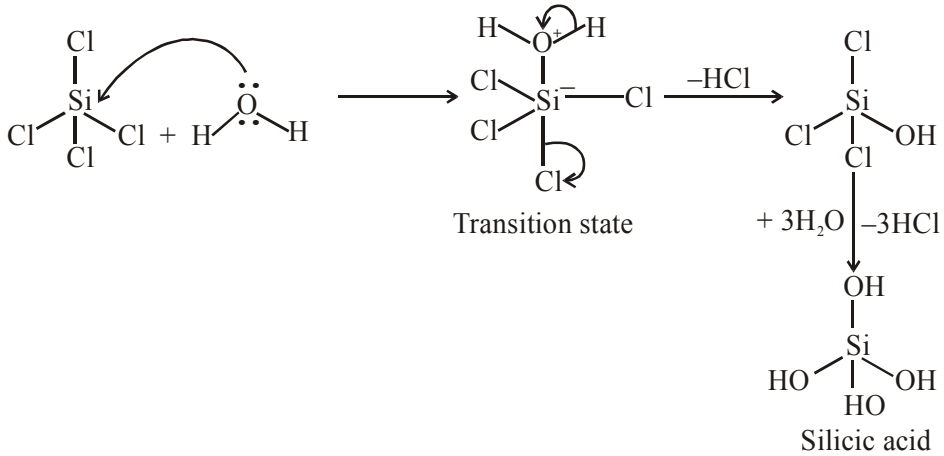
Structure :



HYDROLYSIS :

In hydrolysis of covalent molecules the nucleophilic centre of molecule is replaced by OH^- group of water generally through nucleophilic substitution reaction.

Ex. Hydrolysis of $SiCl_4$



Note : CCl_4, NF_3, is inert towards hydrolysis due to the absence of d orbital, but under drastic condition these molecules under goes hydrolysis.

$$CCl_4 + H_2O \xrightarrow{\text{superheated}} COCl_2 + 2HCl$$

Note : Hydrolysis of XeF_2 & XeF_4 takes place through with redox reaction.

$$XeF_2 + H_2O \longrightarrow Xe + 2HF + \frac{1}{2}O_2$$

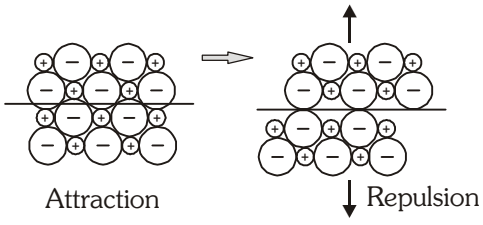
$$3XeF_4 + 6H_2O \longrightarrow 2Xe + XeO_3 + 12HF + \frac{3}{2}O_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

IONIC COMPOUNDS

Properties of ionic compound

(a) Physical state : Ionic compounds are hard, crystalline and brittle due to strong electrostatic force of attraction. Brittleness → {Same charged ions comes nearer. So they repell each other}



(b) Isomorphism : The phenomenon of different ionic compounds, having same crystal arrangement of ions is termed as isomorphism

Condition of Isomorphism :

(i) Same charge on cation & anion between isomorphs

(ii) Same radius ratio range of cation & anion between isomorphs

(iii) Same number of water of crystalization between isomorphs

Ex. (i) $ZnSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$ are isomorphous

(ii) All alums are isomorphous

(c) Boiling point and melting point : Ionic compounds have high boiling point and melting point due to strong electrostatic force of attraction among oppositely charged ions.

(d) Conductivity : It depends on ionic mobility.

(i) In solid state - No free ions - Bad conductor of electricity.

(ii) In fused state or aqueous solution Due to free ions - Good conductor of electricity.

Conductivity order : Solid state < fused state < Aqueous solution

(e) Solubility :

Ionic compounds are more soluble in polar solvalents and less soluble in non polar solvents.

• Solubility of ionic compounds in water mainly depends upon hydration energy & lattice energy.

Q. Why does the solubility of alkaline earth metal hydroxides in water increase down the group?

Ans. Among alkaline earth metal hydroxides, the anion being common the cationic radius will influence the lattice enthalpy. Since lattice enthalpy decreases much more than the hydration enthalpy with increasing ionic size, the solubility increases as we go down the group.

Q. Why does the solubility of alkaline earth metal carbonates and sulphates in water decrease down the group?

Ans. The size of anions being much larger compared to cations, the lattice enthalpy will remain almost constant within a particular group. Since the hydration enthalpies decrease down the group, solubility will decrease as found for alkaline earth metal carbonates and sulphates.

FAJAN'S RULE

Just as all the covalent bonds have some partial ionic character, the ionic bonds also have partial covalent character. The partial covalent character of ionic bonds was discussed by Fajans in terms of the following rules :

- The smaller the size of the cation and the larger the size of the anion, the greater the covalent character of an ionic bond.
- The greater the charge on the cation, the greater the covalent character of the ionic bond.
- For cations of the same size and charge, the one, with electronic configuration $(n-1)d^n ns^0$, typical of transition metals, is more polarising than the one with a noble gas configuration, $ns^2\ np^6$, typical of alkali and alkaline earth metal cations.

- The cation polarises the anion, pulling the electronic charge toward itself and thereby increasing the electronic charge between the two. This is precisely what happens in a covalent bond, i.e., buildup of electron charge density between the nuclei. The polarising power of the cation, the polarisability of the anion and the extent of distortion (polarisation) of anion are the factors, which determine the per cent covalent character of the ionic bond.

$\Rightarrow$ Polarisation power of a cation is usually called ionic potential or charge density.

$$\text{Ionic potential } \phi \text{ (phi)} = \frac{\text{Charge on cation}}{\text{Size of cation}}$$

APPLICATION OF THE CONCEPT OF POLARISATION :

(a) To compare the covalent and ionic character of molecule

(b) To compare the nature of oxide

(c) To compare the electrical conductivity of ionic comopounds

(d) Tendency of the formation of complex compounds

(e) To compare the thermal stability of metal salts

(f) To compare the intensity of colour of compounds

(g) To compare the solubility of heavier metal halide in water.

MOLECULAR ORBITAL THEORY (MOT)

Given by Hunds & Mulliken

(a) Two atomic orbital come nearer & then overlap each other to form two molecular orbitals (MO)

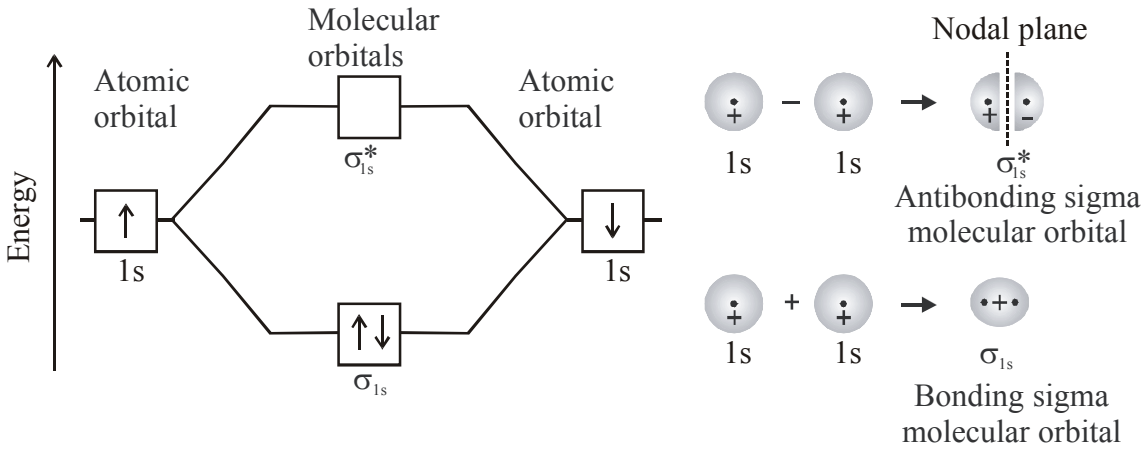
(b) Combination of atomic orbital (AO) forms molecular orbital (MO)

Types of molecular orbitals

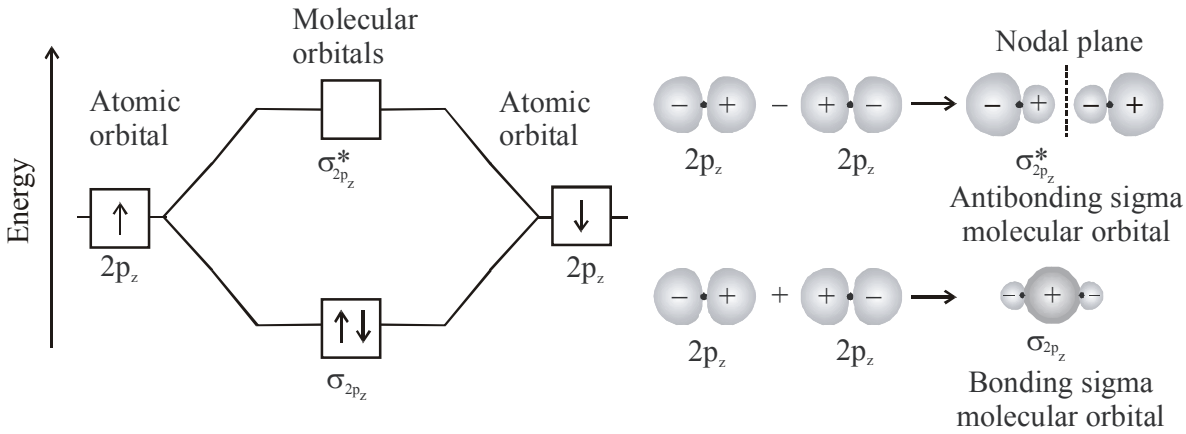
Molecular orbitals of diatomic molecules are designated as σ(sigma), π(pie), δ(delta) etc.

In this nomenclature, the **sigma (σ) molecular orbitals are symmetrical around the inter molecular axis (assumed to be z-axis) while pi (π) molecular orbitals are not symmetrical.**

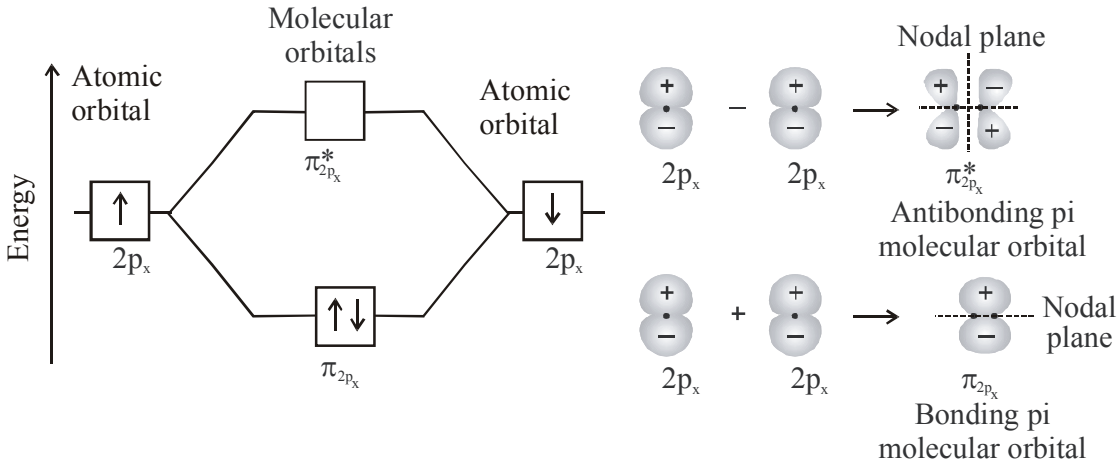
(1) s-s combination of orbitals



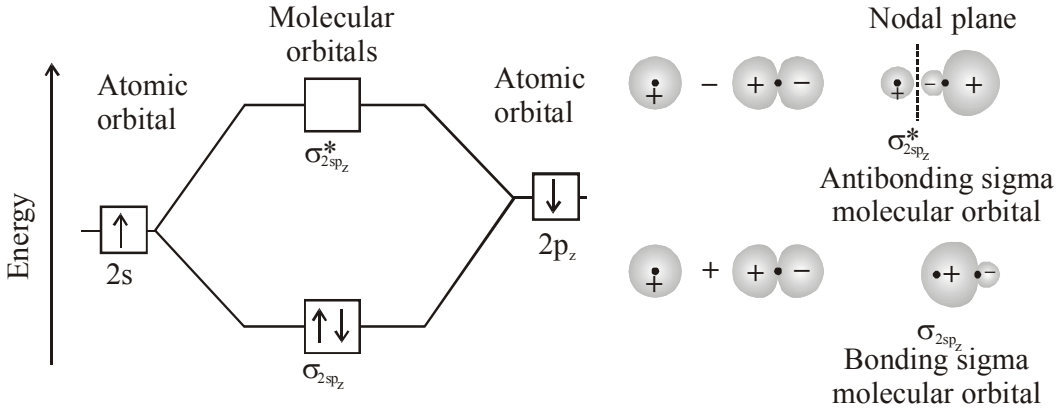
(2) p-p combination of orbitals(end to end overlap)



(3) p-p combination of orbitals (side by side overlap)



(4) s-p combination of orbitals



(c) Energy of BMO < Energy of ABMO.

(d) Molecular orbitals can be filled by electrons according to Aufbau, Hund's, Pauli's principle.

(e) Energy order of the molecular orbitals of homonuclear di-atomic molecules.

Note : Molecular orbital energy diagram for up to N_2 (molecule having ≤ 14 electrons)

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_z} < \pi^*_{2p_x} = \pi^*_{2p_y} < \sigma^*_{2p_z}$$

Note : Molecular orbital energy diagram for O_2 and F_2 (molecule having > 14 electrons)

$$\sigma_{1s} < \sigma^*_{1s} ; < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y} < \pi^*_{2p_x} = \pi^*_{2p_y} < \sigma^*_{2p_z}$$

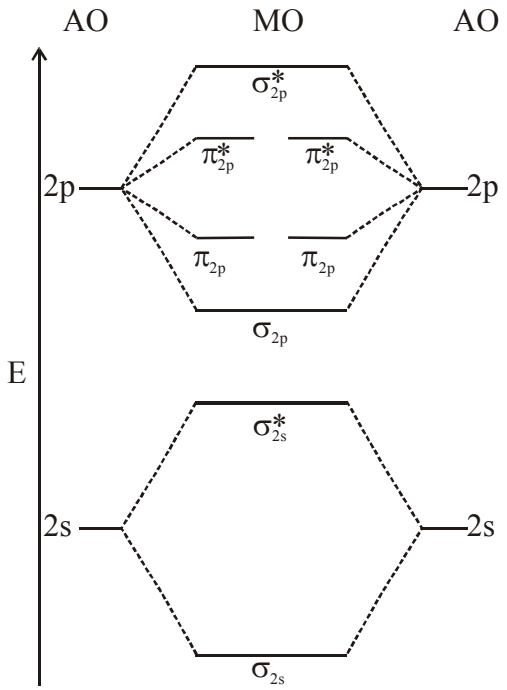
$\sigma *$, $\pi *$ = antibonding molecular orbital

σ, π = bonding molecular orbital

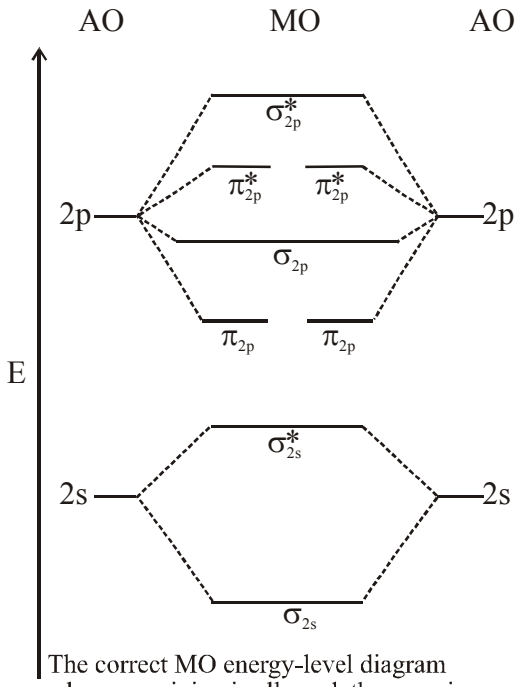
Ex. Why molecular orbitals have different order of energy in N_2 & O_2 ?

Sol. s-p mixing

Hint



The correct MO energy-level diagram when s-p mixing is not allowed.



The correct MO energy-level diagram when s-p mixing is allowed, the energies of the σ_{2p} and π_{2p} orbitals are reversed.

Bond Order

Bond order can be defined as :

$$\textbf{Bond order} = \frac{N_b - N_a}{2}$$

N_b = No. of electron in bonding MO's

N_a = No. of electron in antibonding MO's

- If bond order = 0, it means species does not exist.
- Bond order of 1, 2 & 3 corresponds to a single bond, double & triple bond respectively.
- Bond order ↑ stability of molecule ↑ bond length ↓

Magnetic behaviour

- If the molecule has one or more unpaired electron, it will be paramagnetic,
- If all the electrons are paired it will be diamagnetic.
- Magnetic strength can be calculated by using spin only formula of magnetic moment (μ).
- $\mu = \sqrt{n(n+2)}$ B.M. (where n = number of unpaired electron)

Ex. H_2 = Configuration : $\sigma^2_{(1s)}$, $\sigma^{*0}_{(1s)}$

Bond order = $\frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$, Hence H – H (dimagnetic)

EXERCISE # (O-1)

WEAK FORCES

1. **Statement-1 :** The melting point of noble gases increases as its atomic mass increases.
Statement-2 : Instantaneous dipole induced dipole attraction increases with increase in atomic mass of noble gases.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

2. The critical temperature of water is higher than that of O_2 because the H_2O molecule has :
(A) fewer electrons than O_2 (B) two ionic bonds
(C) V–shape (D) dipole moment

3. Which of the following boiling point order is correct -
(A) $He > T_2 > D_2$ (B) $He < T_2 < D_2$ (C) $T_2 > He > D_2$ (D) $He < D_2 < T_2$

4. Which is the incorrect match for the energy distance function for following interaction -
(A) Debye force : r^{-6} (B) Ion-induced dipole interaction : r^{-2}
(C) London force : r^{-6} (D) Keesom force : r^{-3}

5. Identify the incorrect order of boilng point in the following pair.
(A) $B(OH)_3 < B(OCH_3)_3$ (B) $NF_3 < N(CH_3)_3$
(C) $BF_3 < B(CH_3)_3$ (D) $C_2H_6 < C_2F_6$

BENT'S RULE AND DRAGO'S

6. C–H bond distance is the longest in:
(A) C_2H_2 (B) C_2H_4 (C) C_2H_6 (D) $C_2H_2Br_2$

7. The bond angle and hybridization in ether (CH_3OCH_3) is :
(A) 106°51', sp^3 (B) 104°31', sp^3 (C) 110°, sp^3 (D) None of these

8. Which of the following has been arranged in order of decreasing bond length ?
(A) P–O > Cl–O > S–O (B) P–O > S–O > Cl–O
(C) S–O > Cl–O > P–O (D) Cl–O > S–O > P–O

9. Which is correct statement ?
As the s-character of a hybrid orbital decreases
(I) The bond angle decreases (II) The bond strength increases
(III) The bond length increases (IV) Size of orbital increases
(A) (I), (III) and (IV) (B) (II), (III) and (IV)
(C) (I) and (II) (D) All are correct

10. Among the following, the correct statement is :
(A) Between NH_3 and PH_3, NH_3 is a better electron donor because the lone pair of electrons occupies spherical 's' orbital and is less directional
(B) Between NH_3 and PH_3, PH_3 is a better electron donor because the lone pair of electrons occupies sp^3orbital 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 more 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

11. In which of the following molecule C—C bond length will be highest ?
(A) $CF_3 - CF_3$ (B) $F_2CH - CHF_2$ (C) $FCH_2 - CH_2F$ (D) $CH_3–CF_3$

12. In BClBr I molecule the maximum % s-character provided from the central atom is in bond :
(A) B – I (B) B – Cl (C) B – Br (D) Can not predict

13. Find out the % p-character in the orbital occupied by lone pairs in H_2O.
[$\widehat{HOH}$ = 104°5 and cos (104.5) = –0.25]
(A) 80 % (B) 20 % (C) 70 % (D) 75 %

14. Which of the following order is correct for increasing p-character in orbital used for bonding by central atom
(A) $SiH_4 > CH_4$ (B) $H_2S > H_2O$ (C) $PH_4^+ > PH_3$ (D) $NH_3 > PH_3$

BACK BONDING

15. Boron forms BX_3 type of halides. The correct increasing order of Lewis-acid strength of these halides is
(A) $BF_3 > BCl_3 > BBr_3 > BI_3$ (B) $BI_3 > BBr_3 > BCl_3 > BF_3$
(C) $BF_3 > BI_3 > BCl_3 > BBr_3$ (D) $BF_3 > BCl_3 > BI_3 > BBr_3$

16. Select species which is planar at nitrogen :
(A) $(CH_3)_3N$ (B) $(SiH_3)_3N$ (C) NF_3 (D) NH_3

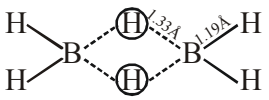
17. Type of back bonding in $(SiH_3)_2O$ is :
(A) $p\pi - d\pi$ (B) $p\pi - p\pi$ (C) $d\pi - d\pi$ (D) None of these

MULTICENTERED BOND

18. The type of overlap in the bridge bond existing in $Al_2(CH_3)_6$ is :-
(A) $sp^3–sp^3d–sp^3$ (B) $sp^3–sp^2–sp^3$ (C) $sp^3–s–sp^3$ (D) $sp^3–sp^3–sp^3$

19. Which one of the following statement is not true regarding diborane?
(A) It has two bridging hydrogens and four perpendicular to the rest.
(B) When methylated, the product is $Me_4B_2H_2$
(C) The bridging hydrogens are in a plane perpendicular to the rest.
(D) All the B–H bond distances are equal.

20. The molecular shape of diborane, is shown:



Consider the following statements for diborane :
(1) Boron is approximately sp^3 hybridised
(2) B–H–B angle is 180°
(3) There are two terminal B–H bonds for each boron atom
(4) There are only 12 bonding electrons available
Of these statements:
(A) 1, 3 and 4 are correct (B) 1, 2 and 3 are correct
(C) 2, 3 and 4 are correct (D) 1, 2 and 4 are correct

SILICATE

21. The number of corners or O-atoms shared per tetrahedron for pyroxene chain silicate is -

(A) 3 (B) 2 (C) 2.5 (D) 1

22. The mineral $Na_2Fe^{II}_3Fe^{III}_2[Si_8O_{22}](OH)_2$ (chrocidolite) is a :

(A) Pyroxene chain silicate (B) Sheet silicate

(C) Amphiboles chain silicate (D) 3D-silicate

23. The silicate anion in the mineral kinoite is a chain of three SiO_4 tetrahedral those share corners with adjacent tetrahedral. The mineral also contains Ca^{2+} ions, Cu^{2+} ions, and water molecules in a 1:1:1 ratio mineral is represented as :

(A) $CaCuSi_3O_{10}.H_2O$ (B) $CaCuSi_3O_{10}.2H_2O$

(C) $Ca_2Cu_2Si_3O_{10}.2H_2O$ (D) none of these

ODD ELECTRON SPECIES

24. Hybridisation related to NO_2 molecule is -

(A) sp^3 (B) sp

(C) sp^3d (D) sp^2

25. In which of the following processes, the magnetic behaviour of the species is changed :-

(A) $2\dot{C}H_3 \longrightarrow C_2H_6$ (B) $2NO_2 \longrightarrow N_2O_4$

(C) $2ClO_3 \longrightarrow Cl_2O_6$ (D) All of these

HYDROLYSIS

26. Which of the following statement is correct ?

(A) BCl_3 is not hydrolysed while $SiCl_4$ can be hydrolysed

(B) CCl_4 is hydrolysed under ordinary condition

(C) XeF_2 produces $Xe(OH)_2$ on hydrolysis

(D) hydrolysis of XeF_2 is a redox reaction

27. **Statement-1 :** Between $SiCl_4$ and CCl_4 only $SiCl_4$ reacts with water at room temperature.

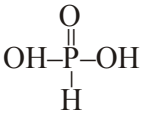
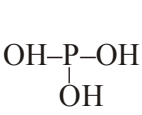
Statement-2 : $SiCl_4$ is ionic and CCl_4 is covalent.

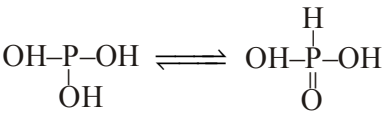
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

28. **Statement-1 :** PCl_3 on hydrolysis gives  and 

Statement-2 : H_3PO_3 exists in two tautomeric forms : 

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

MOLECULE DOES NOT EXIST

29. Which of the following molecule does not exist.

(A) PH_5 (B) NCl_3 (C) NOF_3 (D) XeF_5^-

30. Select non existing specie

(A) PH_3 (B) PH_4^+

(C) $[PF_6]^-$ (D) None of these

INERT PAIR EFFECT

31. **Statement-1 :** Boron does not show univalent nature but unipositive nature of thallium is quite stable.

Statement-2 : Inert pair effect predominates in thallium.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

32. **Statement-1 :** PbI_4 doesn't exist and converts into PbI_2 and I_2 spontaneously at room temperature but $PbCl_4$ needs heating to convert into $PbCl_2$ and Cl_2.

Statement-2 : Pb^{2+} is more stable than Pb^{4+} due to inert pair effect.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

IONIC COMPOUND

33. The dissolution of ionic compounds involves :
(A) Evolution of heat (B) Weakening of attractive forces
(C) Dissociation into ions (D) All of these

34. Select correct order out of given options :
(A) $BeCO_3 < BaCO_3$: Covalent character (B) BeO > SrO : lattice energy
(C) $Be^{2+} < Li^+$: Hydration energy (D) $Be^{2+}(aq.) > Li^+(aq.)$: Ionic mobility

35. The polarizibility of the following ions is/are in the order of
(A) $I^- > Br^- > Cl^- > F^-$ (B) $I^- > Br^- > F^- > C1^-$
(C) $I^- < Br^- < Cl^- < F^-$ (D) $I^- < Br^- < F^- < Cl^-$

36. Which of the following equilibria would have the highest value of K_p at a common temperature?
(A) $MgCO_3 \Leftrightarrow MgO + CO_2$ (B) $CaCO_3 \Leftrightarrow CaO + CO_2$
(C) $SrCO_3 \Leftrightarrow SrO + CO_2$ (D) $BaCO_3 \Leftrightarrow BaO + CO_2$

37. Which of the following set of characteristics lead to the increase in solubility of ionic substances?
(A) High dipole moment, strong attraction by an ion towards solvent and large solvation energy
(B) Low dipole moment, weak attraction by an ion towards solvent and high solvation energy
(C) High dipole moment, strong attraction by an ion towards solvent and low solvation energy
(D) High dipole moment, weak attraction by an ion towards solvent and large solvation energy

38. The solubility of anhydrous $AlCl_3$ and hydrated $AlCl_3$ in diethyl ether are S_1 and S_2 respectively. Then
(A) $S_1 = S_2$ (B) $S_1 > S_2$ (C) $S_1 < S_2$ (D) $S_1 < S_2$ but not $S_1 = S_2$

39. **Statement-1 :** Among alkali metal cations, $Li^+(aq.)$ has highest electrical conductance.
Statement-2 : $Li^+(aq.)$ is largest alkali metal cation because of greater degree of hydration.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

40. **Statement-1 :** $Al(OH)_3$ is amphoteric in nature.
Statement-2 : Al–O and O–H bonds can be broken with equal ease in $Al(OH)_3$.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

MOLECULAR ORBITAL THEORY

41. The bond energy order of He_2^+ and HeH^+ is
(A) $He_2^+ > HeH^+$ (B) $HeH^+ = He_2^+$ (C) $HeH^+ > He_2^+$ (D) Can't be predicted

42. Among KO_2, AlO_2^-, BaO_2 and NO_2^+ unpaired electron is present in :
(A) KO_2 only (B) NO_2^+ and BaO_2 (C) KO_2 and AlO_2^- (D) BaO_2 only

43. During the formation of a molecular orbital from atomic orbitals, probability of electron density is
(A) minimum in the nodal plane (B) maximum in the nodal plane
(C) zero in the nodal plane (D) zero on the surface of the lobe

44. Pick out the **incorrect** statement ?

(A) N_2 has greater dissociation energy than N_2^+

(B) O_2 has lower dissociation energy than O_2^+

(C) Bond length in N_2^+ is less than N_2

(D) Bond length in NO^+ is less than in NO

45. A simplified application of MO theory to the hypothetical molecule 'OF' would give its bond order as :

(A) 2 (B) 1.5 (C) 1.0 (D) 0.5

46. Which of the following is true ?

(A) With increasing Bond order , Bond length decreases & Bond energy increases

(B) With increasing Bond order , Bond length increases & Bond energy decreases

(C) With increasing Bond order , Bond length decreases & Bond energy decreases

(D) With increasing Bond order , Bond length increases & Bond energy increases

47. Which of the following has fractional bond order :

(A) O_2^{2+} (B) O_2^{2-} (C) F_2^{2-} (D) H_2^-

48. **Statement-1:** H_2 molecule is more stable than He–H molecule.

Statement-2 : The antibonding electron in He–H molecule decreases the bond order and there by the stability.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

49. **Statement-1 :** Super oxide ion is paramagnetic whereas peroxide ion is diamagnetic.

Statement-2 : Super oxide ion has one unpaired electron whereas peroxide ion has no unpaired electron.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

50. **Statement-1:** π_b and π^* orbitals obtained from 2p orbital are lying in the same plane.

Statement-2 : Bonding M.O's are formed by constructive interference while antibonding M.O's are formed by destructive interference.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

EXERCISE # (O-2)

WEAK FORCES

1. Which of the following factors are responsible for origination of vander Waals forces ?

(A) Instantaneous dipole-induced dipole interaction

(B) Dipole-induced dipole interaction

(C) Dipole-dipole interaction

(D) Size of molecule

2. Which of the following are true ?

(A) Vander Waals forces are responsible for the formation of molecular crystals

(B) Branching lowers the boiling points of isomeric organic compounds due to decrease in Vander Waals forces of attraction

(C) In graphite, vander Waals forces act between the carbon layers

(D) In diamond, vander Waals forces act between the carbon layers

BENT'S AND DRAGO'S RULE

3. Select the correct statement for following molecules :

(I) $PF_2(CH_3)_3$; **(II)** $PF_2(CF_3)_3$

(A) Both have trigonal bipyramidal structure with respect to P.

(B) P-F bond length is longer in $PF_2(CH_3)_3$ than in $PF_2(CF_3)_3$

(C) F-atoms occupy axial position in both

(D) P-F bond length is lower in $PF_2(CH_3)_3$ than in $PF_2(CF_3)_3$

BACK BONDING

4. Molecules in which bond angle is changed due to back bonding w.r.t B/O/N.

(A) H_3BO_3 (B) $B(OMe)_3$ (C) BF_3 (D) $N(SiH_3)_3$

5. 3dπ-2pπ type back bonding is observed in :

(A) $N(SiH_3)_3$ (B) $\bar{C}Cl_3$ (C) $S(CH_3)_2$ (D) BCl_3

MULTICENTERED BOND

6. No X–X bond exists in which of the following compounds having general form of X_2H_6 ?

(A) B_2H_6 (B) C_2H_6 (C) Al_2H_6 (D) Si_2H_6

7. Three centre - two electron bonds exist in :

(A) B_2H_6 (B) $Al_2(CH_3)_6$ (C) $BeH_2(s)$ (D) $BeCl_2(s)$

8. Select correct statement about B_2H_6

(A) Bridging groups are electron-deficient with 12 valence electrons

(B) It has 2c – 2e B–H bonds

(C) It has 3c – 2e B–H–B bonds

(D) It has 3c – 4e B–H–B bonds

SILICATE

9. In which of the following cases the number of corner shared per tetrahedron is '2' -

(A) Pyroxene chain silicate (B) Amphibole chain silicate

(C) 5-membered cyclic silicate (D) None of these

ODD ELECTRON SPECIES

10. Select correct about NO_2 :

(A) It is odd electron specie (B) N–O bond order = 1.5

(C) Paramagnatic specie (D) Isoelectronic with CO_2

11. The number of specie(s) which are not perfectly planar.

(A) $\dot{C}H_3$ (B) $\dot{C}F_3$ (C) $\dot{C}HF_2$ (D) $\dot{C}H_2F$

12. Which of the following statement is **CORRECT** :-

(A) The free electron of ClO_3 molecule is present in d-orbital of Cl-atom

(B) The free electron of $\dot{C}F_3$ is present in sp^3 hybrid orbital

(C) NO is polar

(D) The free electron of ClO_2 molecule is present in d-orbital of Cl-atom

13. Which of the following statement(s) is / are **INCORRECT** for

$\dot{C}H_3$ = X and $\dot{C}F_3$ = Y

(A) When X dimerises bond angle decreases

(B) When X dimerises bond angle increases

(C) In X–Y molecule C–C bond length less than that in Y–Y molecule

(D) Bond angle in Y is less than X

HYDROLYSIS

14. Which of the following halide(s) cannot be hydrolysed at room temperature

(A) SeF_6 (B) SF_6 (C) CCl_4 (D) NF_3

15. Which of the following statement is/are **INCORRECT** ?

(A) P_4S_{10} gives rise to H_2S gas on hydrolysis

(B) PCl_5 produces $POCl_3$ on partial hydrolysis

(C) H_2SO_5 gives rise to H_2SO_3 on hydrolysis

(D) d-orbital participates in the hydrolysis of SF_6 at room temperature

MOLECULE DOES NOT EXIST

16. Which of the following do/does not exist ?

(A) SH_6 (B) HFO_4 (C) FeI_3 (D) $HClO_3$

17. Which of the following molecule(s) exist-

(A) SF_6 (B) PH_5 (C) PH_3 (D) PCl_5

INERT PAIR EFFECT

18. Which of the following have (18 + 2) electron configuration ?

(A) Pb^{2+} (B) Cd^{2+} (C) Bi^{3+} (D) SO_4^{2-}

19. Which of following stability order is/are correct due to inert pair effect.

(A) $Hg > Hg^{2+}$ (B) $Bi^{3+} < Bi^{5+}$ (C) $Pb^{2+} > Pb^{4+}$ (D) $Fe^{2+} < Fe^{3+}$

IONIC COMPOUND

20. Choose the correct order(s) for the given properties.

(A) $MgSO_4 < SrSO_4 < BaSO_4$: Thermal stability order

(B) $BeC_2O_4 < CaC_2O_4 < BaC_2O_4$: Solubility in water

(C) $LiCl > NaCl > KCl$: Melting point order

(D) $BeF_2 > CaF_2 > SrF_2$: Covalent character order

21. Polarization may be called the distortion of the shape of an anion by an adjacently placed cation. Which of the following statements is/are incorrect :

(A) Minimum polarization is brought about by a cation of low radius

(B) A large cation is likely to bring about a large degree of polarization

(C) Maximum polarization is brought about by a cation of high charge

(D) A small anion is likely to undergo a large degree of polarization

22. Most ionic compounds have :

(A) high melting points and low boiling points

(B) high melting points and nondirectional bonds

(C) high solubilities in polar solvents and low solubilities in nonpolar solvents

(D) three-dimentional network structures, and are good conductors of electricity in the molten state

23. Choose the correct order for the given properties.

(A) $NaF < MgF_2 < AlF_3$: covalent character order.

(B) $NaF < MgF_2 < AlF_3$: melting point order

(C) $NaF < MgF_2 < AlF_3$: lattice energy order

(D) $NaF > MgF_2 > AlF_3$: order of polarising power of cation.

MOLECULAR ORBITAL THEORY

24. Which of the following have identical bond order ?

(A) O_2^{2+} (B) NO^+ (C) CN^- (D) CN^+

25. Which of the following statement is/are correct

(A) The peroxide ion has a bond order of 1 while the oxygen molecule has a bond order of 2

(B) The peroxide ion has a weaker bond than the dioxygen molecule has.

(C) The peroxide ion as well as the dioxygen molecules are paramagnetic

(D) The bond length of the peroxide ion is greater than that of the dioxygen molecule

26. Which of the following statements are true for these given species : N_2, CO, CN^- and NO^+.

(A) All species are paramagnetic (B) The species are isoelectronic

(C) All the species have dipole moment (D) All the species are linear

27. Which of the following have unpaired electron(s)

(A) O_2^+ (B) O_2^- (C) NO (D) H_2^+

28. Which of the following is/are paramagnetic ?

(A) B_2 (B) O_2 (C) N_2 (D) He_2

29. Which of the following species have a bond order of 3 ?

(A) CO (B) CN^- (C) NO^+ (D) O_2^+

30. Which of the following is/are correct ?

(A) During N_2^+ formation, one electron is removed from the bonding molecular orbitals

(B) During O_2^+ formation, one electron is removed from the antibonding molecular orbitals

(C) During O_2^- formation, one electron is added to the bonding molecular orbitals

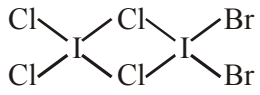
(D) During CN^- formation, one electron is added to the bonding molecular orbitals

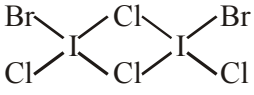
MISCELLANEOUS

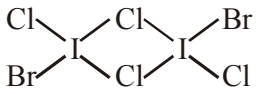
31. Rotation around the bond (between the underlined atoms) is restricted in :

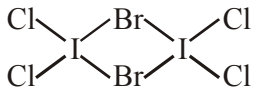
(A) $\underline{C}_2H_4$ (B) $H_2\underline{O}_2$ (C) $\underline{C}_2H_2$ (D) $\underline{C}_2H_6$

32. The experimental result says that two iodine atoms are in different environments and predict the all possible incorrect arrangement for $I_2Cl_4Br_2$.

(A) 

(B) 

(C) 

(D) 

EXERCISE # (S-1)

1. The number of corner of O-atom shared per tetrahedron in 2D-silicate is .....

2. Find the number of angles less than 120° in PH_2F_3.

3. Find the number of molecules which are not having 3c–2e bond from the following.

$Al_2(CH_3)_6$, Si_2H_6 , B_2H_6 , C_2H_6 , Si_2Cl_6 , Al_2Cl_6

4. Find the ratio of π-electrons in the C_2-molecule with that of B_2 molecule according to M.O.T.

5. In which of the following silicates structure, the number of corner/oxygen atoms shared per tetrahedron is '2'.

Pyrosilicate , pyroxene chain silicate ,

2D-silicate , 3D-silicate , 4-membered cyclic silicate

6. The total number of bonding and antibonding electrons in O_2^+ are "....." and "....." respectively.

[If the answer is 14 and 7, then represent as 147]

7. Find the total number of following molecule(s) which have all bond lengths are same.

XeF_4, SF_4, SH_2, NO_3^-, SiF_4, ClF_3, PF_2Cl_3, XeO_3F_2

8. Among the following total number of planar molecules is / are

Cl_2O , $P(CH_3)_3$, $N(CH_3)_3$, ClO_2 , $^{\bullet}CH_3$, NCl_3

9. Calculate the value of "n" in $Zn_nCa_2(Si_3O_{10}).2H_2O$

10. How many compound(s) gives diprotic acid on hydrolysis ?

SO_2Cl_2, $SOCl_2$, $POCl_3$, XeF_2, N_2O_5, P_4O_6, SF_4, BCl_3

EXERCISE # (S-2)

Comprehension # 1 (1 to 3 Questions)

B is the first element of IIIrd group. It forms a number of electron deficient halides and hydrides. Among the hydrides diborane is an important compound.

1. Which of the following halide is the strongest Lewis acid?

(A) BF_3 (B) BCl_3 (C) BBr_3 (D) BI_3

2. Which of the following compounds has $2p\pi - 2p\pi$ bond ?

(A) BF_3 (B) BCl_3 (C) BBr_3 (D) BI_3

3. In B_2H_6 number of 3c – 2e bonds is/are

(A) 1 (B) 2 (C) 3 (D) None

Comprehension # 2 (4 to 6 Questions)

Molecular orbital theory is based on linear combination of atomic orbitals (LCAO). According to LCAO when respective atomic orbitals of the atoms interact, they undergoes constructive and destructive interference giving two types of molecular orbital i.e. bonding and antibonding molecular orbitals respectively.

4. Which of the following specie is paramagnetic ?

(A) NO^- (B) O_2^{2-} (C) CN^- (D) CO

5. Bond order of Be_2 is :

(A) 1 (B) 2 (C) 3 (D) 0

6. Number of anti bonding electrons in N_2 is :

(A) 4 (B) 10 (C) 12 (D) 14

Comprehension # 3 (7 to 8 Questions)

Polarisation of anion in ionic compounds play an important role to influnce the various physical and chemical properties of ionic compound.

7. Amongst LiCl, RbCl, $BeCl_2$ and $MgCl_2$ the compounds with the greatest and the least ionic character, respectively are :

(A) LiCl and RbCl (B) RbCl and $BeCl_2$ (C) RbCl and $MgCl_2$ (D) $MgCl_2$ and $BeCl_2$

8. Compound with maximum ionic character is formed from :

(A) Na and Cl (B) Cs and F (C) Cs and I (D) Na and F

Comprehension # 4 (9 to 10 Questions)

"Hydrolysis is defined as the reaction of water with any susbtance"

9. Choose the correct order of ease of hydrolysis -

(A) $MgCl_2 > AlCl_3$ (B) $SF_6 < SeF_6$ (C) $SnCl_2 > SnCl_4$ (D) None

10. Which of the following oxyacids are formed during the stepwise hydrolysis of P_4O_{10}

(A) tetrametaphosphoric acid (B) tetrapolyphosphoric acid

(C) pyrophosphoric acid (D) All of these

MATCHING LIST

11. Match list I with list II and select the correct answer:

List I (species)	**List II (O-N-O angle)**
(P) NO_2^+	(1) 180°
(Q) NO_2	(2) 134°
(R) NO_2^-	(3) 120°
(S) NO_3^-	(4) 115°
	(5) 109°

	P	**Q**	**R**	**S**		**P**	**Q**	**R**	**S**
(A)	5	4	3	2	(B)	5	2	4	3
(C)	1	2	4	3	(D)	1	4	3	2

12. Match list I with list II and select the correct answer:

List–I (Molecule / Species)	**List–II (Unpaired electron resides in)**
(P) NO_2	(1) d-orbital
(Q) ClO_2	(2) sp^2-orbital
(R) ClO_3	(3) sp^3-orbital
(S) $^{\bullet}CH_3$	(4) p-orbital

Code :

	P	**Q**	**R**	**S**		**P**	**Q**	**R**	**S**
(A)	2	4	1	3	(B)	2	1	3	4
(C)	1	4	2	3	(D)	3	1	2	4

13. Match list I with list II and select the correct answer:

List–I (Process)	**List–II (Operating intraction involved)**
(P) Clathrate compound of Xe in ice	(1) Ion - Dipole
(Q) Liquation of Xe gas	(2) Dipole - Dipole
(R) Liquation of HCl gas	(3) Dipole - Induced dipole
(S) Hydration of Na^+	(4) London forces

Code :

	P	**Q**	**R**	**S**		**P**	**Q**	**R**	**S**
(A)	1	3	4	2	(B)	3	4	1	2
(C)	3	4	2	1	(D)	1	3	2	4

MATRIX MATCH

14. Match the column

Column-I (Compounds given)	**Column-II (Characteristics associated with given compounds)**
(A) $BeCl_2$	(P) Undergoes partial hydrolysis
(B) SiF_4	(Q) All possible bond angles are identical
(C) SO_2Cl_2	(R) Hydrolysed product of the attacking site is electron deficient and finally produces polymerised product
(D) BF_3	(S) Maximum number of atoms present in one plane is three

15. Match the column

Column-I (Molecules)	**Column-I (Characteristics given among the molecules of column-I)**
(A) CH_4	(P) Molecule is having perfect tetrahedral shape
(B) CH_2F_2	(Q) C-F bond has maximum p-character
(C) CHF_3	(R) C–H bond has maximum s-character
(D) CF_4	(S) Molecule is having maximum number of equal angles
	(T) Molecule has lowest bond angle

16. Match the column

Column-I Processes	**Column-II Correct characteristics**
(A) $N_2^+ \longrightarrow N_2$	(P) Magnetic moment gets changed
(B) $Zn^{2+} \longrightarrow Zn$	(Q) The process is associated with two electronic change
(C) $O_2^{2-} \longrightarrow 2O^{2-}$	(R) Magnetic behaviour gets changed
(D) $C_2^{2-} \longrightarrow C_2$	(S) Electron(s) associated in the process enter(s) into π^*_{2p} orbital
	(T) Electron(s) associated in the process involve(s) σ_{2p} orbital

Answer Q.17 to Q.19 by appropriately matching the information given in the three columns of the following table

Molecular Orbital	Number of nodal plane	Symmetry of Molecular Orbital
(1) σ_s	(P) 3	(I) BMO, gerade
(2) π_p	(Q) 2	(II) ABMO, ungerade
(3) $\sigma^*_{p_z}$	(R) 1	(III) BMO, ungerade
(4) δ^*	(S) 0	(IV) ABMO, gerade

17. Which of the following matching is **INCORRECT.**

(A) (1), S, I (B) (2), R, I (C) (3), R, II (D) (4), P, II

18. How many orbitals are occupied with set (1)(S)(I) in F_2

(A) 0 (B) 1 (C) 2 (D) 3

19. If z axis is the molecular axis then **CORRECT** matching for $d_{xy} + d_{xy}$ orbital is 4, P, II for the substraction of wave function.

Which of the following matching is **CORRECT** for the addition of wave function for same combination of orbitals.

(A) P, IV (B) P, III (C) Q, II (D) Q, I

EXERCISE # J-MAIN

1. The bond order in NO is 2.5 while that in NO^+ is 3. Which of the following statement is true for these two species ? **[AIEEE–2004]**

(1) Bond length in NO^+ is equal to that NO (2) Bond length in NO is greater than NO^+

(3) Bond length in NO^+ is greater than NO (4) Bond length is unpredictable

2. The states of hybridization of boron and oxygen atoms in boric acid (H_3BO_3) are respectively **[AIEEE–2004]**

(1) sp^3 and sp^2 (2) sp^2 and sp^3 (3) sp^2 and sp^2 (4) sp^3 and sp^3

3. The maximum number of 90° angles between bond pair-bond pair of electrons is observed in :- **[AIEEE–2004]**

(1) dsp^2 hybridization (2) sp^3d hybridization

(3) dsp^3 hybridization (4) sp^3d^2 hybridization

4. Which one of the following specie is diamagnetic in nature ? **[AIEEE-2005]**

(1) He_2^+ (2) H_2 (3) H_2^+ (4) H_2^-

5. Which of the following molecule\ion does not contain unpaired electrons? **[AIEEE-2006]**

(1) N_2^+ (2) O_2 (3) O_2^{2-} (4) B_2

6. Among the following mixtures, dipole-dipole as the major interaction, is present in **[AIEEE-2006]**

(1) KCl and water (2) benzene and carbon tetrachloride

(3) benzene and ethanol (4) acetonitrile and acetone

7. A metal, M forms chlorides in its +2 and +4 oxidation states. Which of the following statement about these chlorides is correct ? **[AIEEE-2006]**

(1) MCl_2 is more ionic than MCl_4

(2) MCl_2 is more easily hydrolysed than MCl_4

(3) MCl_2 is more volatile than MCl_4

(4) MCl_2 is more soluble in anhydrous ethanol than MCl_4

8. The decreasing values of bond angles from NH_3 (106°) to SbH_3 (91°) down group-15 of the periodic table is due to **[AIEEE-2006]**

(1) decreasing lp – bp repulsion (2) increasing electronegativity

(3) increasing bp – bp repulsion (4) increasing p-orbital character in sp^3

9. In which of the following ionization process, the bond order has increased and the magnetic behaviour has changed **[AIEEE-2007]**

(1) $NO \rightarrow NO^+$ (2) $O_2 \rightarrow O_2^+$ (3) $N_2 \rightarrow N_2^+$ (4) $C_2 \rightarrow C_2^+$

10. Which of the following species exhibits the diamagnetic behaviour **[AIEEE-2007]**

(1) t_A^+ (2) O_2 (3) NO (4) t_A^{A-}

11. which one of the following pairs of species have the same bond order? **[AIEEE-2008]**

(1) CN^- and NO^+ (2) $CN^-$and CN^+ (3) O_2^- and CN^- (4) NO^+ and CN^+

12. The bond dissociation energy of B–F in BF_3 is 646 kJ mol^{-1} whereas that of C–F in CF_4 is 515 kJ mol^{-1}. The correct reason for higher B–F bond dissociation energy as compared to that of C–F is :- **[AIEEE-2009]**

(1) Significant $p\pi - p\pi$ interaction between B and F in BF_3 whereas there is not possibility of such interaction between C and F in CF_4.

(2) Lower degree of $p\pi - p\pi$ interaction between B and F in BF_3 than that between C and F in CF_4

(3) Smaller size of B-atom as compared to that of C-atom

(4) Stronger σ bond between B and F in BF_3 as compared to that between C and F in CF_4

13. Using MO theory predict which of the following species has the shortest bond length ?**[AIEEE-2009]**

(1) O_2^- (2) O_2^{2-} (3) O_2^{2+} (4) O_2^+

14. Among the following the maximum covalent character is shown by the compound :- **[AIEEE-2011]**

(1) $AlCl_3$ (2) $MgCl_2$ (3) $FeCl_2$ (4) $SnCl_2$

15. Which one of the following molecules is expected to exhibit diamagnetic behaviour ?

(1) C_2 (2) N_2 (3) O_2 (4) S_2 **[AIEEE-2013]**

16. In which of the following pairs of molecules/ions, both the species are not likely to exist ?

(1) H_2^+, He_2^{2-} (2) H_2^-, He_2^{2-} (3) H_2^{2+}, He_2 (4) H_2^-, He_2^{2+} **[JEE-M-2013]**

17. Stability of the species Li_2, Li_2^- and Li_2^+ increases in the order of :- **[JEE-M-2013]**

(1) $Li_2 < Li_2^+ < Li_2^-$ (2) $Li_2^- < Li_2^+ < Li_2$ (3) $Li_2 < Li_2^- < Li_2^+$ (4) $Li_2^- < Li_2 < Li_2^+$

18. Which one of the following properties is **not** shown by NO ? **[JEE-M-2014]**

(1) It combines with oxygen to form nitrogen dioxide

(2) It's bond order is 2.5

(3) It is diamagnetic in gaseous state

(4) It is a neutral oxide

19. The correct order of thermal stability of hydroxides is : **[JEE-M-2015 (on line)]**

(1) $Ba(OH)_2 < Sr(OH)_2 < Ca(OH)_2 < Mg(OH)_2$

(2) $Mg(OH)_2 < Sr(OH)_2 < Ca(OH)_2 < Ba(OH)_2$

(3) $Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

(4) $Ba(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Mg(OH)_2$

20. Which of the alkaline earth metal halides given below is essentially covalent in nature :- **[JEE-M-2015 (on line)]**

(1) $SrCl_2$ (2) $CaCl_2$ (3) $BeCl_2$ (4) $MgCl_2$

21. Which one of the following alkaline earth metal sulphates has its hydration enthalpy greater than its lattice enthalpy ? **[JEE-M-2015]**

(1) $BaSO_4$ (2) $SrSO_4$ (3) $CaSO_4$ (4) $BeSO_4$

22. The intermolecular interaction that is dependent on the inverse cube of distance between the molecules is :- **[JEE-M-2015]**

(1) London force (2) Hydrogen bond
(3) ion-ion interaction (4) ion-dipole interaction

23. Which one has the highest boiling point ? **[JEE-M-2015]**

(1) Kr (2) Xe (3) He (4) Ne

24. Which intermolecular force is most responsible in allowing xenon gas to liquefy? **[JEE (MAIN) ONLINE 2016]**

(1) Ionic
(2) Instantaneous dipole- induced dipole
(3) Dipole - dipole
(4) Ion - dipole

25. The bond angle H–X–H is the greatest in the compound : **[JEE (MAIN) ONLINE 2016]**

(1) NH_3 (2) H_2O (3) PH_3 (4) CH_4

26. Which of the following species is not paramagnetic :- **[JEE-MAINS-2017]**

(1) NO (2) CO (3) O_2 (4) B_2

27. Which of the following is paramagnetic ? **[JEE-MAINS-2017 (On-line)]**

(1) CO (2) O_2^{2-} (3) NO^+ (4) B_2

28. sp^3d^2 hybridization is not displayed by : **[JEE-MAINS-2017 (On-line)]**

(1) $[CrF_6]^{3-}$ (2) BrF_5 (3) PF_5 (4) SF_6

29. The number of S=O and S–OH bonds present in peroxodisulphuric acid and pyrosulphuric acid respectively are : **[JEE-MAINS-2017 (On-line)]**

(1) (2 and 4) and (2 and 4) (2) (4 and 2) and (2 and 4)
(3) (2 and 2) and (2 and 2) (4) (4 and 2) and (4 and 2)

30. The correct sequence of decreasing number of π-bonds in the structures of H_2SO_3, H_2SO_4 and $H_2S_2O_7$ is:- **[JEE-MAINS-2017 (On-line)]**

(1) $H_2S_2O_7 > H_2SO_4 > H_2SO_3$ (2) $H_2SO_3 > H_2SO_4 > H_2S_2O_7$
(3) $H_2S_2O_7 > H_2SO_3 > H_2SO_4$ (4) $H_2SO_4 > H_2S_2O_7 > H_2SO_3$

31. The increasing order of the boiling points for the following compounds is:- **[JEE-MAINS-2017 (On-line)]**

(I) C_2H_5OH (II) C_2H_5Cl (III) $C_2H_5CH_3$ (IV) $C_2H_5OCH_3$

(1) (III) < (II) < (I) < (IV) (2) (II) < (III) < (IV) < (I)
(3) (IV) < (III) < (I) < (II) (4) (III) < (IV) < (II) < (I)

32. The number of P–OH bonds and the oxidation state of phosphorus atom in pyrophosphoric acid ($H_4P_2O_7$) respectively are :- **[JEE-MAINS-2017 (On-line)]**

(1) five and four (2) five and five (3) four and five (4) four and four

33. The group having triangular planar structures is :- **[JEE-MAINS-2017 (On-line)]**

(1) CO_3^{2-}, NO_3^-, SO_3 (2) NCl_3, BCl_3, SO_3 (3) NH_3, SO_3, CO_3^{2-} (4) BF_3, NF_3, CO_3^{2-}

34. Which of the following are Lewis acids ? **[JEE-MAINS-2018]**
(1) $AlCl_3$ and $SiCl_4$ (2) PH_3 and $SiCl_4$ (3) BCl_3 and $AlCl_3$ (4) PH_3 and BCl_3

35. According to molecular orbital theory, which of the following will not be a viable molecule ? **[JEE-MAINS-2018]**
(1) He_2^+ (2) H_2^- (3) H_2^{2-} (4) He_2^{2+}

36. Which of the following compounds contain(s) no covalent bond(s) ? **[JEE-MAINS-2018]**
KCl, PH_3, O_2, B_2H_6, H_2SO_4
(1) KCl, H_2SO_4 (2) KCl (3) KCl, B_2H_6 (4) KCl, B_2H_6, PH_3

37. In KO_2, the nature of oxygen species and the oxidation state of oxygen atom are, respectively **[JEE-MAINS-2018 (Online]**
(1) Superoxide and –1/2 (2) Oxide and -–2
(3) Peroxide and –1/2 (4) Superoxide and –1

38. Which of the following best describes the diagram below of a moleuclar orbital ?

[JEE-MAINS-2018 (Online]
(1) An antibonding π orbital (2) An antibonding σ orbital
(3) A non-bonding orbital (4) A bonding π orbital

39. In the molecular orbital diagram for the molecular ion, N_2^+, the number of electrons in the σ_{2p} molecular orbital is :- **[JEE-MAINS-2018 (Online]**
(1) 3 (2) 1 (3) 0 (4) 2

40. Xenon hexafluoride on partial hydrolysis produces compounds 'X' and 'Y' Compounds 'X' and 'Y' and the oxidation state of Xe are respectively : **[JEE-MAINS-2018 (Online]**
(1) XeO_2F_2(+6) and XeO_2(+4) (2) $XeOF_4$(+6) and XeO_2F_2(+6)
(3) $XeOF_4$(+6) and XeO_3(+6) (4) XeO_2(+4) and XeO_3(+6)

41. Which of the following is a lewis acid ? **[JEE-MAINS-2018 (Online]**
(1) NaH (2) NF_3 (3) PH_3 (4) $B(CH_3)_3$

42. A group 13 element 'X' reacts with chlorine gas to produce a compound XCl_3. XCl_3 is electron deficient and easily reacts with NH_3 to form $Cl_3X \leftarrow NH_3$ adduct; however, XCl_3 does not dimerize. X is :- **[JEE-MAINS-2018 (Online]**
(1) Ga (2) Al (3) In (4) B

43. Which of the following conversions involves change in both shape and hybridisation ? **[JEE-MAINS-2018 (Online]**
(1) $BF_3 \rightarrow BF_4^-$ (2) $H_2O \rightarrow H_3O^+$ (3) $CH_4 \rightarrow C_2H_6$ (4) $NH_3 \rightarrow NH_4^+$

EXERCISE # J-ADVANCE

1. The molecules that will have dipole moment are : **[IIT–1992]**
(A) 2, 2–dimethylpropane (B) trans-pent-2-ene
(C) cis-hex-3-ene (D) 2, 2, 3, 3–tetramethylbutane

2. Which of the following have identical bond order ? **[IIT–1992]**
(A) CN^- (B) O_2^- (C) NO^+ (D) CN^+

3. Among the following the one that is polar and has the central atom with sp^2 hybridisation is :
(A) H_2CO_3 (B) SiF_4 (C) BF_3 (D) $HClO_2$ **[IIT–1997]**

4. Which of the following is soluble in water ? **[IIT 98]**
(A) CS_2 (B) C_2H_5OH (C) CCl_4 (D) $CHCl_3$

5. The correct order of hybridization of the central atom in the following species NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 is : **[IIT 2001]**
(A) dsp^2, sp^3d, sp^2 and sp^3 (B) sp^3, dsp^2, sp^3d, sp^2
(C) dsp^2, sp^2, sp^3, sp^3d (D) dsp^2, sp^3, sp^2, sp^3d

6. The common features among the species CN^-, CO and NO^+ are : **[IIT 2001]**
(A) bond order three and isoelectronic (B) bond order three and weak field ligands
(C) bond order two and π - acceptors (D) isoelectronic and weak field ligands

7. Which of the following molecular specie has unpaired electron(s) ? **[JEE 2002]**
(A) N_2 (B) F_2 (C) O_2^- (D) O_2^{2-}

8. According to molecular orbital theory which of the following statement about the magnetic character and bond order is correct regarding O_2^+ **[JEE 2004]**
(A) Paramagnetic and Bond order < O_2 (B) Paramagnetic and Bond order > O_2
(C) Diamagnetic and Bond order < O_2 (D) Diamagnetic and Bond order > O_2

9. Among the following, the paramagnetic compound is **[JEE 2007]**
(A) Na_2O_2 (B) O_3 (C) N_2O (D) KO_2

10. The species having bond order different from that in CO is **[JEE 2007]**
(A) NO^- (B) NO^+ (C) CN^- (D) N_2

11. **Statement-1 :** In water, orthoboric acid behaves as a weak monobasic acid. **[JEE 2007]**
Statement-2 : In water, orthoboric, acid acts as a proton donor.
(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(C) Statement-1 is True, Statement-2 is False.
(D) Statement-1 is False, Statement-2 is True.

12. **Statement-1 :** Pb^{+4} compounds are stronger oxidizing agents than Sn^{4+} compounds **[JEE 2008]**
Statement-2 : The higher oxidation states for the group 14 elements are more stable for the heavier members of the group due to 'inert pair effect' .
(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(C) Statement-1 is True, Statement-2 is False.
(D) Statement-1 is False, Statement-2 is True.

13. Match each of the diatomic molecules/ions in Column I with its property / properties in Column II. **[JEE 2009]**

Column I	**Column II**
(A) B_2	(P) Paramagnetic
(B) N_2	(Q) undergoes oxidation
(C) O_2^-	(R) Undergoes reduction
(D) O_2	(S) Bond order ≥ 2
	(T) Mixing of 's' and `p' orbitals

14. In the reaction **[JEE 2009]**

$$2X + B_2H_6 \longrightarrow [BH_2(X)_2]^+ [BH_4]^-$$

the amine(s) X is (are)

(A) NH_3 (B) CH_3NH_2 (C) $(CH_3)_2NH$ (D) $(CH_3)_3N$

15. The species having pyramidal shape is **[JEE 2010]**

(A) SO_3 (B) BrF_3 (C) SiO_3^{2-} (D) OSF_2

16. Assuming that Hund's rule is violated, the bond order and magnetic nature of the diatomic molecule B_2 is **[JEE 2010]**

(A) 1 and diamagnetic (B) 0 and diamagnetic (C) 1 and paramagnetic (D) 0 and paramagnetic

Subjective

17. The value of n in the molecular formula $Be_nAl_2Si_6O_{18}$ is **[JEE 2010]**

18. The total number of diprotic acids among the following is **[JEE 2010]**

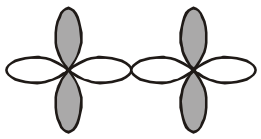
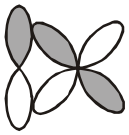
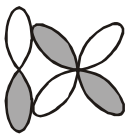
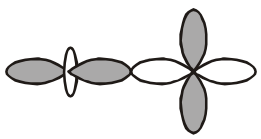
H_3PO_4 H_2SO_4 H_3PO_3 H_2CO_3 $H_2S_2O_7$
H_3BO_3 H_3PO_2 H_2CrO_4 H_2SO_3

19. Among the following, the number of elements showing only one non-zero oxidation state is
O, Cl, F, N, P, Sn, Tl, Na, Ti **[JEE 2010]**

20. Assuming 2s-2p mixing is NOT operative, the paramagnetic species among the following is : **[JEE Adv. 2014]**

(A) Be_2 (B) B_2 (C) C_2 (D) N_2

21. Match the orbital overlap figures shown in **List-I** with the description given in **List-II** and select the correct answer using the code given below the lists. **[JEE Adv. 2014]**

List-I	**List-II**
(P) 	(1) p – d π antibonding
(Q) 	(2) d – d σ bonding
(R) 	(3) p – d π bonding
(S) 	(4) d – d σ antibonding

Code :

	P	Q	R	S
(A)	2	1	3	4
(C)	2	3	1	4

	P	Q	R	S
(B)	4	3	1	2
(D)	4	1	3	2

22. Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing product formed is - **[JEE Adv. 2015]**

23. When O_2 is adsorbed on a metallic surface, electron transfer occurs from the metal to O_2. The **TRUE**, statement (s) regarding this adsorption is (are) **[JEE Adv. 2015]**

(A) O_2 is physisorbed (B) heat is released

(C) occupancy of π^*_{2p} of O_2 is increased (D) bond length of O_2 is increased

24. According to Molecular Orbital Theory, **[JEE Adv. 2016]**

(A) C_2^{2-} is expected to be diamagnetic

(B) O_2^{2+} is expected to have a longer bond length than O_2

(C) N_2^+ and N_2^- have the same bond order

(D) He_2^+ has the same energy as two isolated He atoms

25. The colour of the X_2 molecules of group 17 elements changes gradually from yellow to violet down the group. This is due to - **[JEE Adv. 2017]**

(A) the physical state of X_2 at room temperature changes from gas to solid down the group

(B) decrease in HOMO-LUMO gap down the group

(C) decrease in π^*-σ^* down the group

(D) decrease in ionization energy down the group

26. Among H_2, He_2^+, Li_2, Be_2, B_2 ,C_2, N_2, O_2^-, and F_2 , the number of diamagnetic species is - (Atomic number) : H = 1, He = 2, Li = 3, Be = 4, B = 5, C = 6, N = 7, O = 8 , f = 9) **[JEE Adv. 2017]**

27. The sum of the number of lone pairs of electrons on each central atom in the following species is. **[JEE Adv. 2017]**

$[TeBr_6]^{2-}$, $[BrF_2]^+$, SNF_3 and $[XeF_3]^-$

[Atomic number : N = 7, F = 9, S = 16, Br = 35, Te = 52, Xe = 54]

28. The option(s) with only amphoteric oxides is (are): **[JEE Adv. 2017]**

(A) Cr_2O_3, CrO, SnO, PbO (B) NO, B_2O_3, PbO, SnO_2

(C) Cr_2O_3, BeO, SnO, SnO_2 (D) ZnO, Al_2O_3, PbO, PbO_2

29. Among the following, the correct statement(s) is are **[JEE Adv. 2017]**

(A) $Al(CH_3)_3$ has the three-centre two-electron bonds in its dimeric structure

(B) $AlCl_3$ has the three-centre two-electron bonds in its dimeric structure

(C) BH_3 has the three-centre two-electron bonds in its dimeric structure

(D) The Lewis acidity of BCl_3 is greater than that of $AlCl_3$

30. Based on the compounds of group 15 elements , the correct statement(s) is (are) **[JEE Adv. 2018]**

(A) Bi_2O_5 is more basic than N_2O_5

(B) NF_3 is more covalent than BiF_3

(C) PH_3 boils at lower temperature than NH_3

(D) The N–N single bond is stronger than the P–P single bond

ANSWERS KEY

EXERCISE # O-1

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A	D	D	B	A	C	C	B	A	C
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	C	A	C	B	B	B	A	D	D	A
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	B	C	C	D	D	D	C	A	A	D
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	A	B	D	B	A	A	A	B	D	C
Que.	41	42	43	44	45	46	47	48	49	50
Ans.	C	A	C	C	B	A	D	A	A	B

EXERCISE # O-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A, B, C	A, B, C	A, B, C	A, B, D	A, B	A, C	A, B, C	B, C	A, C	A,B,C
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	B,C,D	B,C,D	B,C	B, C, D	C, D	A, B, C	A, C, D	A, C	A, C	A, D
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	A, B, D	B, C, D	A, B, C	A, B, C	A, B, D	B, D	A,B,C,D	A, B	A, B, C	A, B, D
Que.	31	32								
Ans.	A, B, C	B,C,D								

EXERCISE # S-1

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	3	8	4	2	2	105	4	3	2	4

EXERCISE # S-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	D	A	B	A	D	A	B	B	B	D
Que.	11	12	13	14				15		
Ans.	C	B	C	(A)–Q,R,S (B)–P,Q,S (C)–S (D)–P,Q				(A)–P,S (B)–Q,T (C)–R (D)–P,S		
Que.	16					17	18	19		
Ans.	(A) – P,R,T (B) – Q (C) – Q (D) – Q,T					B	C	D		

EXERCISE # J-MAINS

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	2	3	4	2	3	4	1	4	1	4
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	1	1	3	1	2	3	2	3	3	3
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	4	2	2	2	4	2	4	1 & 3	4	1
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	4	3	1	3	3	2	1	1	2	2
Que.	41	42	43							
Ans.	4	4	1							

EXERCISE # J-ADVANCE

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	B, C	A, C	A	B	B	A	C	B	D	A
Que.	11	12	13					14	15	16
Ans.	C	C	(A)-P,Q,R,T(B)-Q,R,S,T(C)-P,Q,R(D)-P,Q,R,S					B, C	D	A
Que.	17	18	19	20	21	22	23	24	25	26
Ans.	3	6	2	C	C	6	B,C,D	A,C	B, C	5 or 6
Que.	27	28	29	30						
Ans.	6	C, D	A, C, D	A, B, C						

CO-ORDINATION CHEMISTRY

☐ INTRODUCTION :

(a) The concept of co-ordination compounds arises from the complex formation tendency of transition elements.

(b) These compounds play a vital role in our lives, as chlorophyll of plants, vitamin B_{12} and haemoglobin of animal blood are the co-ordination compounds of Mg, Co and Fe respectively.

(c) The co-ordination compounds play important role in analytical chemistry , polymerisation reactions, metallurgy and refining of metals, photography, water purification etc.

(d) Co-ordination compounds also find many applications in electroplating, textile dyeing and medicinal chemistry.

☐ ADDITION COMPOUNDS :

When solutions containing two or more salts in simple molecular proportion are evaporated, crystals of new compound separate out.

These compounds are called molecular or addition compounds.

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

$CuSO_4 + 4NH_3 + H_2O \longrightarrow [Cu(NH_3)_4]SO_4 \cdot H_2O$

These addition compounds can be divided into two classes :

(A) DOUBLE SALTS :

Those which lose their identity in solution

In solutions these compounds break down into simpler ions. Such addition compounds which lose their identity in solutions are called **double salts** .

Example :

Potash alum $K_2SO_4 \cdot Al_2(SO)_4)_3 \cdot 24H_2O$ when dissolved in water breaks down into K^+, ra_t^{A-}, Al^{+3} ions and therefore is an example of **double salt**.

(B) COORDINATION COMPOUNDS :

Those which retain their identity in solution.

In aqueous solution, these addition compounds do not furnish all simple ions but instead give more complex ions having complicated structure .

Example :

Potassium ferrocyanide $K_4[Fe(CN)_6]$ does not furnish simple K^+, Fe^{2+} and CN^- ions but gives K^+ ions and complex ferrocyanide ions, $[Fe(CN)_6]^{4-}$. These types of compounds are called **complex compounds or co-ordination compounds**.

On the basis of stability of complex ion, complex ions are further divided as follows –

(i) Perfect complexes : The compounds in which complex ion is fairly stable and further dissociation or feebly dissociation is not possible in solution state.

Ex. $K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$

$\downarrow$

$Fe^{2+} + 6CN^-$ (Feebly dissociated)

The ferrocyanide ion $[Fe(CN)_6]^{4-}$ is so insignificantly dissociated that it can be considered as practically undissociated and does not give the qualitative test of Fe^{2+} or CN^- ions..

(ii) Imperfect complexes : Those complexes in which complex ion is less stable and is reversibly dissociated to give enough simple ions and thus respond to their usual qualitative test.

Ex. $K_2[Cd(CN)_4] \longrightarrow 2K^+ + [Cd(CN)_4]^{2-}$

$\Downarrow\Uparrow$

$Cd^{2+} + 4CN^-$ (appreciably dissociated)

☐ DEFINITIONS OF TERMS USED IN CO-ORDINATION COMPOUNDS

(a) **Co-ordination or complex compound :** Co-ordination compounds are those molecular compounds which retain their identity even when dissolved in water or any other solvent and their properties are completely different from those of the constituent ions.

(b) **Central ion :** The cation to which one or more neutral molecules or ions are attached is called the atom / ion. Since, the central ion acts as an acceptor and thus has to accommodate electron pairs donated by the donor atoms of neutral molecules or ions, it must have empty orbitals of appropriate energy.

(c) **Complex ion :** A complex ion may be defined as an electrically charged radical which is formed by the combination of a simple cation with one/more neutral molecules or one/more simple.

(d) **Co-ordination number :** The total number of co-ordinate covalent bond formed by central metal in complex is called the co-ordination number of the central metal ion .

Some common co-ordination number of important metals are as given below.

Metal	Coordination Number	Metal	Coordination Number
Cu^{+}	2, 4	Ni^{2+}	4, 6
Ag^{+}	2	Fe^{2+}	4, 6
Au^{+}	2, 4	Fe^{3+}	6
Hg_2^{2+}	2	Co^{2+}	4, 6
Cu^{2+}	4, 6	Co^{3+}	6
Ag^{2+}	4	Al^{3+}	6
Pt^{2+}	4	Sc^{3+}	6
Pd^{2+}	4	Pt^{4+}	6
Mg^{2+}	6	Pd^{4+}	6

Example. Coordination number of the central metal ions in

(i) $[Cu(NH_3)_4]^{2+}$ is four (ii) $[Fe(EDTA)]^{-}$ is six

(e) **Co-ordination sphere :** The part of the complex enclosed in square bracket is known as co-ordination sphere. It is actually combination of central metal and ligands.

(f) **Ligands :**

(a) The ions or neutral molecules which combine with central metal ion to form complex are called ligands.

(b) They act as electron pair donor (i.e. Lewis bases) though certain ligands also accept electron from central metal and such ligands are known as π - acid ligands.

❖ CLASSIFICATION OF LIGANDS

(A) Based on charge

(i) Neutral ligands : H_2O, NO, CO, C_6H_6 etc.
(ii) Positive ligands : NO^+, $N_2H_5^+$
(iii) Negative ligands : Cl^-, NO_2^-, CN^-, OH^-

(B) Based on denticity

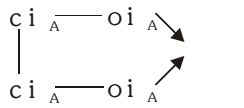
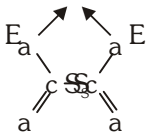
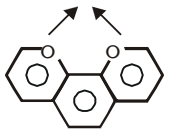
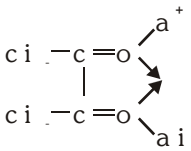
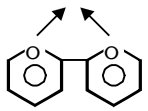
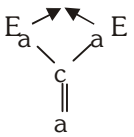
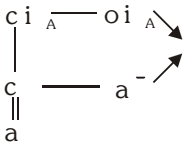
The number of electron pairs donated to central metal by a particular ligand is known as DENTICITY. Depending on number of electron pairs donated, these are classified in following categories.

(a) Unidentate/monodentate ligands

Ligands which donate one pair of electron to the central metal are called unidentate ligands. X^-, CN^-, NO_2^-, NH_3, Pyridine, OH^-, NO_3^-, H_2O, SO_3^{-2}, CO, NO, OH^-, O^{-2}, $(C_6H_5)_3P$ etc.

(b) Bidentate ligands

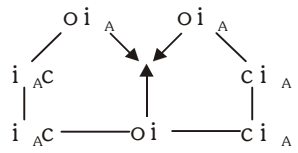
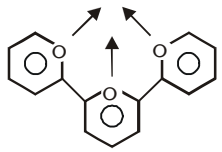
Ligands which have two donor atoms and have the ability to link with central metal ion at two positions are called bidentate ligands.

(c) Tridentate ligands

The ligands which donate three pairs of electrons to the central metal are called tridentate ligands

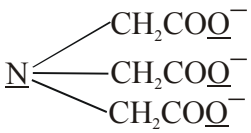
Example.

(d) Tetradentate ligands

Those ligands which can donate four electron pairs to the central metal are known as tetradentate ligands,

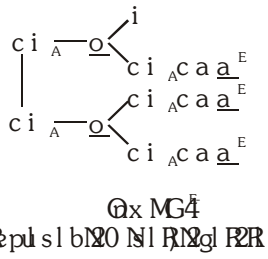
Example : (Underline atoms are donating atom)



Nitrilotriacetato (nta^{3-})

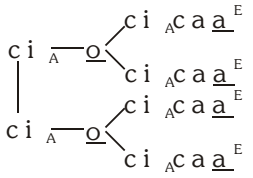
(e) Pentadentate ligands : Those ligands which can five electron pairs to the central metal are known as pentadentate ligands.

Example : Ethylenediamine triacetate ion. (Underline atoms are donating atom)



(f) Hexadentate ligands : Those ligands which can donate six electron pairs to the central metal are known as hexadentate ligands.

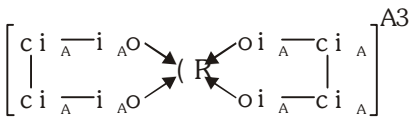
Example : (Underline atoms are donating atom)



(g) Chelating ligands

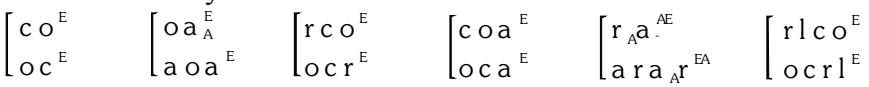
Polydentate ligands whose structures permit the attachment of two or more donor site to metal ion simultaneously, thus resulting in cyclic structure are called chelating ligands and compound formed is known as **chelate compound**.

Example :



(h) Ambidentate ligands

Ligands which can ligate through two different atoms present in it are called ambidentate ligands. At a time only one atom can donate.



Example :

CN^- can coordinate through either the nitrogen or the carbon atom to central metal ion.

(i) Flexidentate ligands

Ligands which sometimes do not use all the donor sites to get coordinated with central metal ion are known as flexidentate ligands.

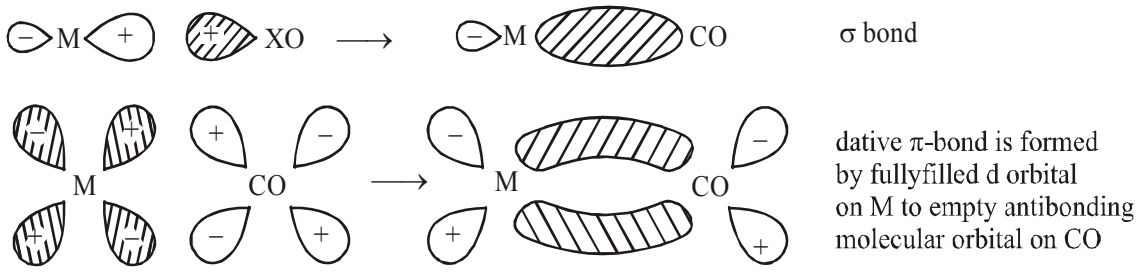
Ex. etc.

(C) Based upon bonding interaction between the ligand and the central atom.

(i) Classical or simple ligand : These ligand only donate the lone pair of electrons to the central atom.
eg. : O^{2-}, OH^-, F^- etc.

(ii) Non classical or π-acid or π-acceptor ligand : These ligand not only donate the lone pair of electrons to central metal but also accept the electron cloud from central atom
eg. : CO, CN^-, NO^+, PF_3, PR_3 etc.

BONDING IN METAL CARBONYL : **Ex.** $[Fe(CO)_5]$; $[Ni(CO)_4]$; $[Cr(CO)_6]$



Schematic diagram of orbital overlaps in metal carbonyls.

(a) The metal-carbon bond in metal carbonyls may be represented as the donation of an electron pair from carbon to vacant orbital of metal & form σ bond (M ⟵ CO).

(b) A second bond is formed by back bonding sometimes called dative π-bonding. This is arises from side ways overlap of a full orbital on the metal with the empty antibonding π^*p_y/π^*p_z (if x-axis is molecular axis) molecular orbital of the carbon monooxide, thus forming a π M $\xrightarrow{b\pi-\pi}$ CO. bond (dπ-pπ back bond).

(c) The filling or partial filling, of the antibonding orbital on CO reduces the bond order of C–O bond from the triple bond in CO towards a double bond. This shown by the increase in C–O bond length from 1.128Å in CO to about 1.15 Å in many carbonyls.

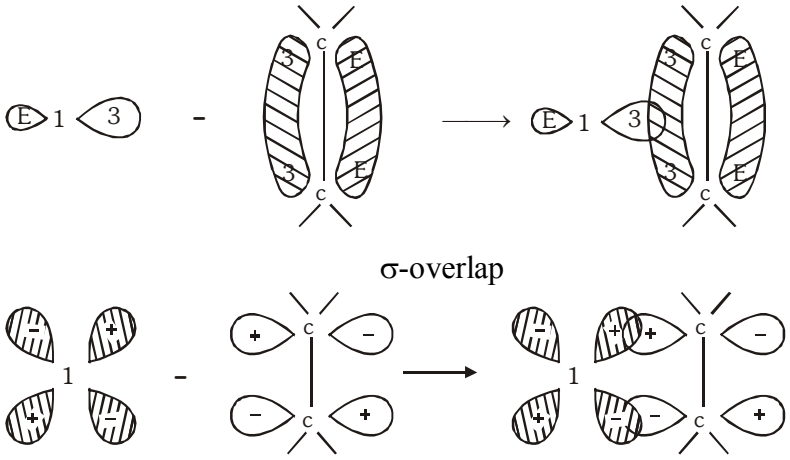
(d) Since CO accept the back donated electrons from the metal atom in to its vacant π* orbital, CO is called π-acid or π-acceptor ligand or π-bonding ligand. Other such π-acid ligands are– CN^-, RCN, $^{3}_{o}a$.

Note:- π-acid ligands like PF_3, PPh_3 $AsCl_3$ etc. accept the back donated electrons from the metal atom in to its vacant d-orbital of central atom.

Bonding in π-bonded organo metallic compound. Like zeises salt K [Pt $Cl_3(\pi\text{-}C_2H_4)$]

The bonding of alkenes to a transition metal to form complexes has two components. First, the π-electron density of the alkene overlaps with a σ-type vacant orbital or the metal atom.

Second is the π back bond formed by the flow of electron density from a filled d-orbital on the metal into the vacant π^*-antibonding molecular orbital on the alkene molecule as shown below :



☐ IUPAC NOMENCLATURE OF COORDINATION COMPOUNDS

The main rules of naming of complexes are –

(a) Like simple salts, the positive part of the coordination compound is named first.

Ex. $K_4[Fe(CN)_6]$ the naming of this complex starts with potassium.

$[Cr(NH_3)_6]Cl_3$ the naming of this complex starts with name of complex ion.

(b) Naming of coordination sphere :- The names of ligands along with their numerical prefixes (to represent their no) are written first, followed by the name of central metal.

(c) The ligands can be neutral, anionic or cationic.

(i) The neutral ligands are named as the molecule **Ex**. C_5H_5N pyridine, $(C_6H_5)_3P$ Triphenyl phosphine.

H_2N — CH_2—CH_2—NH_2 ethylene diamine.

The neutral ligands which are not named as the molecule are CO carbonyl, NO nitrosyl, H_2O Aqua, NH_3 ammine.

(ii) Anionic ligands ending with 'ide' are named by replacing the 'ide' with suffix 'O'.

Symbol	Name as ligand	Symbol	Name as ligand
Cl^-	Chloro/Chlorido	N^{3-}	Nitrido
Br^-	Bromo/Bromido	O_2^{2-}	Peroxo/Peroxido
CN^-	Cyano/Cyanido	O_2H^-	Perhydroxo/Perhydroxido
O^{2-}	Oxo/Oxido	S^{2-}	Sulphido
OH^-	Hydroxo/Hydroxido	NH^{2-}	Imido
H^-	Hydrido/Hydrido	NH_2^-	Amido

Ligands whose names end in 'ite' or 'ate' become 'ito' i.e., by replacing the ending 'e' with 'o' as follows.

Symbol	Name as ligand	Symbol	Name as ligand
CO_3^{2-}	Carbonato	SO_3^{2-}	Sulphito
$C_2O_4^{2-}$	Oxalato	CH_3COO^-	Acetato
SO_4^{2-}	Sulphato	ONO^-	(bonded through oxygen) nitrito
NO_3^-	Nitrato	NO_2^-	(bonded through nitrogen) nitro
$S_2O_3^{-2}$	Thiosulphato		

(iii) Positive ligands naming ends in 'ium' NH_2—NH_3^+ Hydrazinium, NO^+ nitrosonium/nitrosylium.

(d) If ligands are present more than once, then their number is indicated by prefixes like di, tri, tetra etc.

(e) If words like di, tri, tetra are already used in the naming of ligand, or if it is polydented ligand or organic ligand, the prefixes bis–, tris– tetrakis–, pentakis– etc. are used to specify their number.

Example : $[Pt(en)_2Cl_2]Cl_2$: Dichlorobis(ethylenediamine)platinum(IV) chloride.

(f) When more than one type of ligands are present in the complex, then the ligands are named in the alphabetical order.

(g) After naming of ligands the central metal ion is to be named followed by its oxidation state in Roman numbers in brackets. (as per IUPAC)

If the complex is neutral or provides a cationic complex ion, then the central metal ion is to be named as it is.

If the complex provides anionic complex ion then the name of central metal ion ends with 'ate'

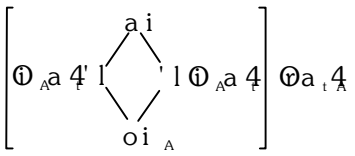
Example : $(NH_4)_2[CuCl_4]$: Ammonium tetrachloridocuprate(II)

(h) After the naming of central metal ion, anion which is in the outer sphere is to be named. The naming of some of the complexes is done as follows – (as per IUPAC)

	Complex Compounds	IUPAC Name
(i)	$K_4[Fe(CN)_6]$ (anionic complex) so suffix 'ate' is added with metal name	Potassium hexacyanoferrate(II)
(ii)	$K_2[PtCl_6]$	Potassium hexachloridoplatinate(IV)
(iii)	$[Co(NH_3)_6]Cl_3$ (Cationic complex) so metal is without any suffix	Hexamminecobalt(III) chloride
(iv)	$[Cr(H_2O)_4Cl_2]Cl$	Tetraaquadichloridochromium(III) chloride
(v)	$[Pt(NH_3)_2Cl_4]$	Diamminetetrachloridoplatinum(IV)
(vi)	$[Co(NH_3)_3Cl_3]$ (Neutral complex) So no suffix is used with metal ion	Triamminetrichloridocobalt(III)
(vii)	$K_3[Co(NO_2)_6]$	Potassium hexanitrocobaltate(III)
(viii)	$Na_3[Fe(CN)_5NO]$	Sodium pentacyanonitrosylferrate(II)
(ix)	$[NiCl_4]^{-2}$	Tetrachloridonickelate(II) ion
(x)	$[Ru(NH_3)_5Cl]^{+2}$	Pentamminechloridoruthenium(III) ion
(xi)	$[Fe(en)_3]Cl_3$	Tris(ethylenediamine)iron(III) chloride
(xii)	$[Ni(Gly)_2]$	Bis(glycinato)nickel(II)

(i) If a complex ion has two metal atoms then it is termed polynuclear. The ligand which connects the two metal ions is called as **Bridging ligand or Bridge group**.

A prefix of Greek letter μ, is repeated before the name of each different kind of bridging group.



FORMATION OF CO-ORDINATION COMPOUNDS

It can be explained by number of theories.

(A) Werner's co-ordination theory

(B) Sidwick theory or Effective Atomic Number Theory (EAN)

(C) Valence bond theory

(D) Crystal field theory

(A) WERNER'S CO-ORDINATION THEORY :

Werner's co-ordination theory was the first attempt to explain the bonding in co-ordination compounds. The main postulates of this theory are :

(a) Metals possesses two types of valencies - Primary valency and secondary valency.

(b) Primary valencies are normally ionisable and are exhibited by a metal in the formation of its simple salts such as $CoCl_3$, $CuSO_4$ and AgCl. In these salts the primary valencies of Co, Cu and Ag are 3, 2, 1 respectively. Primary valencies are referred to as oxidation state of their metal ion.

(c) Secondary valencies are non-ionisable and are exhibited by a metal in the formation of its complex ions such as $[Co(NH_3)_6]^{3+}$, $[Cu(NH_3)_4]^{2+}$ and $[Ag(NH_3)_2]^{+}$. In these complex, the secondary valencies of Co^{3+}, Cu^{2+}, Ag^{+} are 6, 4 and 2 respectively. These are refered to as co-ordination number (C.N.) of the metal cation.

(d) Primary linkages (valencies) are satisfied by negative ions while secondary valencies are satisfied by neutral molecules, negative ions or in some cases positive ions also.

(e) Every metal atom or ion has a fixed number of secondary valencies. In other words, the co-ordination number of the metal atom is usually fixed.

(f) Every metal has tendency to satisfy both its primary and secondary valencies.

(g) The ligands satisfying secondary valency are always directed towards fixed positions in space about the central metal atom or ion. Thus, the co-ordination compounds have a definite geometry. Werner deduced that in $CoCl_3 \cdot 5NH_3$ only two of the three chlorine atoms are ionic and 5 NH_3 and one Cl form co-ordinate bonds to Co^{3+} ion.

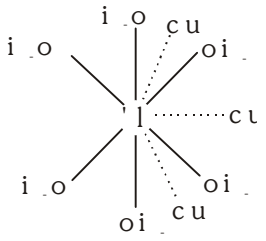
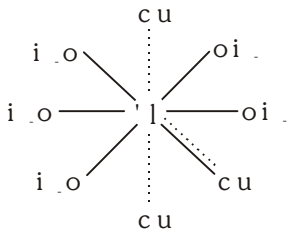
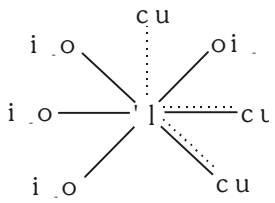
Formula of some cobalt complexes.

Example :

	Old	New	No. of Cl^- Ions precipitated	Total No. of ions
(i)	$CoCl_3 \cdot 6\ NH_3$	$[Co(NH_3)_6]Cl_3$	3	4
(ii)	$CoCl_5 \cdot 5\ NH_3$	$[Co(NH_3)_5Cl]Cl_2$	2	3
(iii)	$CoCl_3 \cdot 4\ NH_3$	$[Co(NH_3)_4Cl_2]Cl$	1	2

Complex	Modern formula	No. of Cl^- Ions precipitated	Total number of ions
$PtCl_4 . 6NH_3$	$[Pt(NH_3)_6]Cl_4$	4	5
$PtCl_4 . 5NH_3$	$[Pt(NH_3)_5Cl]Cl_3$	3	4
$PtCl_4 . 4NH_3$	$[Pt(NH_3]_4Cl_2]Cl_2$	2	3
$PtCl_4 . 3NH_3$	$[Pt(NH_3)_3Cl_3]Cl$	1	2
$PtCl_4\ 2NH_3$	$[Pt(NH_3)_2Cl_4]$	0	0 (non-electrolyte)

❖ **WERNER'S REPRESENTATION OF COMPLEXES**

(i)	$Fe(NH_3)_6Cl_3$		$[Fe(NH_3)_6]Cl_3$ Dotted lines indicate primary valency and continuous lines indicate secondary valency of metal ion.
(ii)	$Fe(NH_3)_5Cl_3$		$[Fe(NH_3)_5Cl]Cl_2$ In this complex two 'Cl' groups act as primary valencies and one of the 'Cl' acts as secondary valency also.
(iii)	$Fe(NH_3)_4Cl_3$		$[Fe(NH_3)_4Cl_2]Cl$ In this complex one 'Cl' group act as primary valency and two of the 'Cl' groups act as secondary valencies also.

(B) SIDWICK THEORY OR EFFECTIVE ATOMIC NUMBER CONCEPT (EAN)

Sidwick proposed effective atomic number theory to explain the stability of the complexes. Total number of electrons on central metal including those tranferred from ligands is known as EAN. The EAN generally coincides with the atomic number of next inert gas except in some cases.

EAN can be calculated by the following relation :

EAN = (atomic number of the metal – oxidation state of central metal with sign) + number of electrons gained from the donor atoms of the ligands.

Example Effective atomic number of the metal atom in the following :

(a) $K_3[Cr(C_2O_4)_3]$ is 33 (b) $K_4[Fe(CN)_6]$ is 36

(C) VALENCE BOND THEORY

The main features of this theory are -

(a) Every metal ion when it forms a complex compound undergoes formation of coordinate covalent bond.

(b) During this bond formation, the metal ion acts as electron pair acceptor. For this the metal ion provides vacant orbitals.

(c) The number of vacant orbitals provided is equal to the coordination number of metal ion.

Example : In the formation of $[Fe(NH_3)_6]^{3+}$, Fe^{+3} ion provides six vacant orbitals.

In $[Cu(NH_3)_4]^{2+}$, Cu^{+2} ion provides four vacant orbitals.

(d) The metal provides vacant orbitals only after the process of hybridisation, thus vacant hybrid orbitals are provided by the metal ion.

(e) The vacant hybrid orbitals of metal ion get overlapped by orbitals of ligands containing lone pair of electrons.

(f) The number of such overlappings is equal to the coordination number of metal ion.

(g) The empty 'd' orbitals involved in hybridisation may be inner (n-1)d or outer "nd" orbitals and accordingly complexes are called as **Inner orbital complexes** and **outer orbital complexes** respectively.

(h) In certain complexes pairing of electrons takes place in ligand field, resulting in decrease in spin only magnetic moment, such complexes are known as Low spin complexes

(i) $\text{Bohr magneton} = \dfrac{eh}{4\pi mc}$

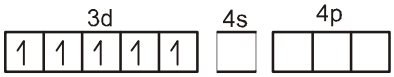
(j) Paramagnetism is represented in the term of spin only magnetic moment.

$\mu = \sqrt{s(s+2)}$ B.M. n = Number of unpaired electron

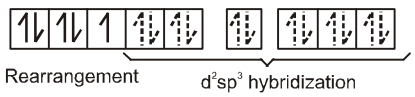
Example $[Fe(CN)_6]^{3-}$ is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic.

Sol. $[Fe(CN)_6]^{3-}$ involves d^2sp^3 hybridization.

Fe^{3+}, $[Ar]\ 3d^5$



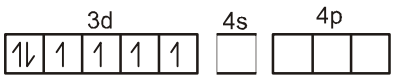
$[Fe(CN)_6]^{3-}$



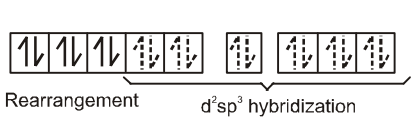
One d-orbital is singly occupied, hence it is weakly paramagnetic in nature.

$[Fe(CN)_6]^{4-}$ also involves d^2sp^3 hybridization but it has Fe^{2+} ion as central ion.

Fe^{2+}, $[Ar]\ 3d^6$

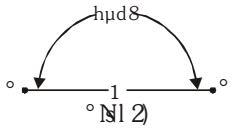
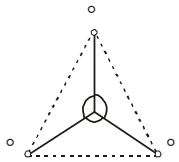
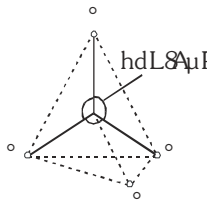
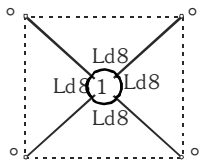
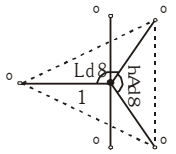
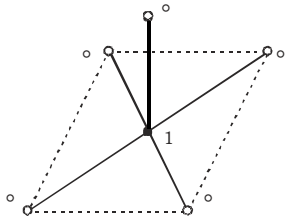
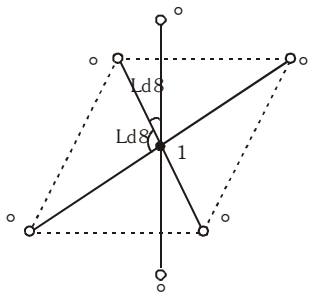


$[Fe(CN)_6]^{4-}$



All electrons are paired, hence it is diamagnetic in nature.

Some Example :

Coordination Number	Hybridised orbitals	Geometrical shape of the Complex	Examples of Complex
2	sp		$[Ag(NH_3)_2]^+$ $[Ag(CN)_2]^-$
3	sp^2		$[HgI_3]^-$
4	sp^3		$[CuCl_4]^{-2}$ $[ZnCl_4]^{-2}$ $[FeCl_4]^-$ $[Ni(CO)_4]$ $[Zn(NH_3)_4]^{+2}$
4	dsp^2 ($d = d_{x^2-y^2}$)		$[PdCl_4]^{2-}$ $[Ni(CN)_4]^{2-}$ $[Pt(NH_3)_4]^{+2}$ $[Cu(NH_3)_4]^{+2}$ $[PtCl_4]^{2-}$
5	sp^3d ($d = d_{z^2}$) or dsp^3 ($d = d_{z^2}$)		$[Fe(CO)_5]$ $[CuCl_5]^{3-}$
5	sp^3d ($d = d_{x^2-y^2}$) or dsp^3 ($d = d_{x^2-y^2}$)	 Square pyramidal	$[Ni(CN)_5]^{-3}$
6	d^2sp^3 (inner orbital complex) or sp^3d^2 (outer orbital complex) in both case d-orbitals are d_{z^2} & $d_{x^2-y^2}$.		$[Cr(NH_3)_6]^{+3}$ $[Ti(H_2O)_6]^{+3}$ $[Fe(CN)_6]^{-3}$ $[Co(NH_3)_6]^{+3}$ $[PtCl_6]^{-2}$,$[CoF_6]^{-3}$

- **Drawback of valence bond theory :**
  (a) It describes bonding in co-ordination compounds only qualitatively but not account for the relative stabilities for different co-ordination complexes.
  (b) It does not offer any explanation for optical absorption spectra (coloration) of complexes
  (c) It does not describe the detailed magnetic properties of co-ordination compounds.

(D) CRYSTAL FIELD THEORY : The drawbacks of VBT of coordination compounds are, to a considerable extent, removed by the Crystal Field Theory.

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interaction between the metal ion and the ligand. Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules. The five d-orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of polar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lost. It results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystal field.

(a) Crystal field splitting in octahedral coordination entities :

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in d orbitals of metal and the electrons (or negative charges) of the ligands. Such a repulsion is more when the d orbitals of metal are directed towards the ligand than when it is away from the ligand.

Thus, the $d_{x^2-y^2}$ and d_{z^2} orbitals (axial orbitals) which point towards the axis along the direction of the ligand will experience more repulsion and will be raised in energy ; and the d_{xy} , d_{yz} and d_{zx} orbitals (non-axial) orbitals which are directed between the axis will be lowered in energy relative to the average energy in the spherical crystal field.

Thus, the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as crystal field splitting and the energy separation is denoted by Δ_0 (the subscript o is for octahedral). Thus, the energy of the two e_g orbitals will increase by $(3/5)\Delta_0$ and that of the three t_{2g} will decrease by $(2/5)\ \Delta_0$.

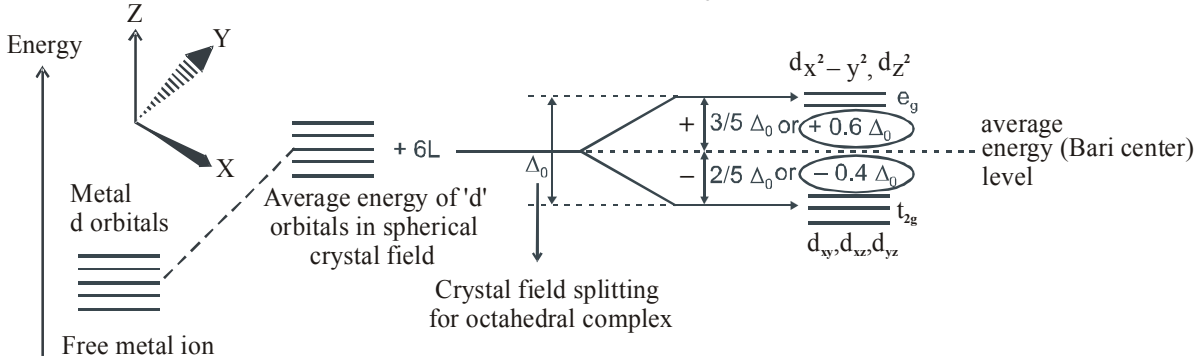


Figure showing crystal field splitting in octahedral complex.

The crystal field splitting, Δ_0, depends upon the fields produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below :

$I^- < Br^- < SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < CN^- < CO$

Note : In SCN^-, S is donating atom and in NCS^-, N is donating atom.

Such a series is termed as spectrochemical series. It is an experimentally determined series based on the absorption of light by complexes with different ligands. For d^4 configuration, the fourth electron will singly occupy e_g orbital (according to Hund's rule) or will undergo pairing in t_{2g} orbital, which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting, Δ_0 and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two possibilites are :

(i) If $\Delta_0 < P$, the fourth electron enters in one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_0 < P$ are known as weak field ligands and form high spin complexes.

(ii) If $\Delta_0 > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as strong field ligands and form low spin complexes.

Crystal Field stabilising energy in Octahedral field :

Formula : $CFSE = [-0.4\ n_{t_{2g}} + 0.6\ n_{e_g}]\ \Delta_0 + xP$.

Where $n_{t_{2g}}$ & n_{e_g} are number of electron(s) in t_{2g} & e_g orbitals respectively and Δ_0 crystal field splitting energy for octahedral complex. "x" represents the number of electron pairs and P is mean pairing energy.

(b) Crystal field splitting in tetrahedral coordination entities :

In tetrahedral coordination entity formation, the d orbital splitting is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\Delta_0$. This may attributes to the following two reasons.

(i) There are only four ligands instead of six, so the ligand field is only two thirds the size ; as the ligand field spliting is also the two thirds the size and (ii) the direction of the orbitals does not concide with the direction of the ligands. This reduces the crystal field spliting by roughly further two third. So $\Delta_t = \frac{2}{3} \times \frac{2}{3} = \frac{4}{9}\Delta_o$.

Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

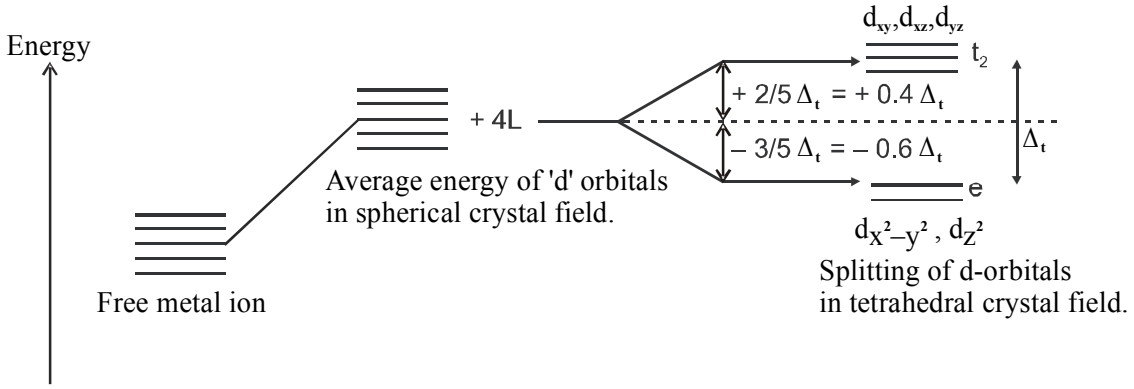


Figure showing crystal field splitting in tetrahedral complex.

Since $\Delta_t < \Delta_o$ crystal field spliting favours the formation of octahedral complexes.

Crystal Field stabilising energy in Tetrahedral field :

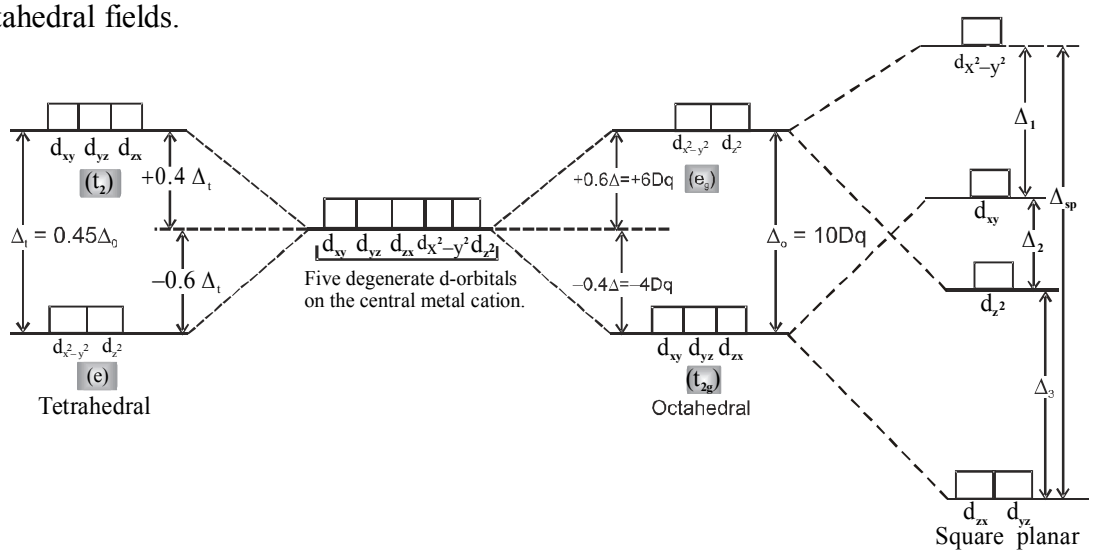
Formula : CFSE = $[-0.6\ n_e + 0.4\ n_{t_2}]\ \Delta_t + xP$.

where n_{t_2} & n_e are number of electron(s) in t_2 & e orbitals respectively and Δ_t crystal field splitting energy for tetrahedral complex. "x" represents the number of electron pairs and P is mean pairing energy.

(c) Crystal field splitting in square planar co-ordination entities :

The square planar arrangement of ligands may be considered to be one derived from the octahedral field by removing two trans-ligands located along the Z-axis. In the process, the e_g and t_{2g} sets of orbitals is lifted i.e., these orbitals will no longer be degenerate.

The four ligands in square planar arrangement around the central metal ion are shown in Fig. As the ligands approach through the x and y axis, they would have greatest influence on $d_{x^2-y^2}$ orbital, so the energy of this orbital, will be raised most. The d_{xy} orbital, lying in the same plane, but between the ligands will also have a greater energy though the effect will be less than that on the $d_{x^2-y^2}$ orbitals. On the other hand, due to absence of ligands along Z-axis, the d_{z^2} orbital becomes stable and has energy lower than that of d_{xy} orbital. Similarly d_{yz} and d_{xz} become more stable. The energy level diagram may be represented as shown in figure along with tetrahedral and octahedral fields.



The value of Δ_{sp} has been found larger than Δ_o because of the reason that d_{xz} and d_{yz} orbitals interact with only two ligands in the square planar complexes, while in octahedral complexes the interaction takes place only with four ligands. Δ_{sp} has been found equal to $1.3\Delta_o$. Thus.

$\Delta_{sp} = (\Delta_1 + \Delta_2 + \Delta_3) > \Delta_o$ and $\Delta_{sp} = 1.3\ \Delta_o$.

(E). STABILITY OF COORDINATION COMPOUNDS :

The stability of a coordination compound $[ML_n]$ is measured in terms of the stability constant (equilibrium constant) given by the expression,

$$\beta_n = [ML_n]/[M(H_2O)_n][L]^n$$

for the overall reaction :

$$M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O$$

By convention, the water displaced is ignored, as its concentration remains essentially constant. The above overall reaction takes place in steps, with a stability (formation) constant, K_1, K_2, K_3, ... K_n for each step as represented below :

$$M(H_2O)_n + L \rightleftharpoons ML(H_2O)_{n-1} + H_2O$$

$$K_1 = [ML(H_2O)_{n-1}] / \{[M(H_2O)_n][L]\}$$

$$ML_{n-1}(H_2O) + L \rightleftharpoons ML_n + H_2O$$

$$K_n = [ML_n] / \{[ML_{n-1}(H_2O)][L]\}$$

$$M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O$$

$$\beta_n = K_1 \times K_2 \times K_3 \times ..... \times K_n$$

β_n, the stability constant, is related to thermodynamic stability when the system has reached equilibrium. Most of the measurements have been made from aqueous solutions, which implies that the complex is formed by the ligand displacing, water from the aqua complex of the metal ion. Ignoring the charge and taking L as an unidentate ligand, the stepwise formation of the complex is represented as shown above.

K_1, K_2, K_3 ..... K_n representing the stepwise stability (or formation) constants.

The above is thermodynamic stability criteria, there can be another kind of stability called kinetic stability, which measures the rate of ligand replacement.

(F). FACTORS INFLUENCING THE MAGNITUDE OF C.F.S.E. :

1. **Different charges on the cation of the same metal :** The cation with a higher oxidation state has a larger value of CFSE than that with lower oxidation state e.g.,

$$[Fe(H_2O)_6]^{3+} > [Fe(H_2O)_6]^{2+}$$

2. **Same charges on the cation but the number of d-electrons is different :** The metal cation the magnitude of CFSE with the increase of the number of d-electrons, e.g.,

$$[Co(H_2O)_6]^{2+} < [Ni(H_2O)_6]^{2+}$$

3. **Quantum number (n) of the d-orbitals of the central metal ion :** As 'n' increase CFSE increases.

$$[Co(NH_3)_6]^{3+} < [Rh(NH_3)_6]^{3+} < [Ir(NH_3)_6]^{3+}$$

4. **Types of Hybridisation :**

$$\Delta_t = \frac{4}{9}\Delta_0$$

5. **Presence of cheleting ligand increases CFSE :**

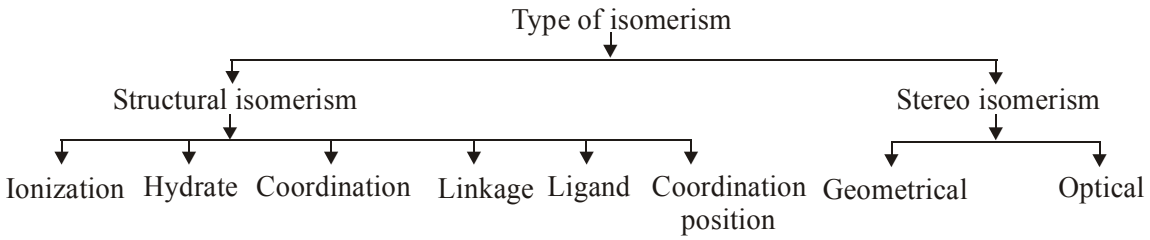
$$[Fe(Ox)_3]^{3-} > [Fe(SCN)_6]^{3-}$$

☐ ISOMERISM IN COMPLEXES

(a) Compounds which have the same molecular formula, but differ in their properties due to the difference in structure are called as **Isomers**.

(b) Isomerism is commonly considered, to be the characteristic of only organic compounds, it is also found although less frequently among inorganic substances.

❖ CLASSIFICATION OF ISOMERISM



(A) Structural isomerism

It arises due to the difference in the type of chemical linkages and distribution of ligands within and outside the coordination sphere.

(a) **Ionisation isomerism**

The type of isomerism which is due to the exchange of groups or ions between the coordination sphere and the ionisation sphere.

Example. (i) $Co(NH_3)_4Br_2SO_4$ can be represented as

$[Co(NH_3)_4Br_2]SO_4$ (red violet) and $[Co(NH_3)_4SO_4]Br_2$ (red)

These complexes give sulphate ion and bromide ion respectively

(ii) $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

(iii) $[Co(NH_3)_4(NO_3)_2]SO_4$ and $[Co(NH_3)_4SO_4](NO_3)_2$

(b) **Hydrate isomerism**

This type of isomerism is due to presence of different number of water molecules inside a coordination sphere.

Example. $Cr(H_2O)_6Cl_3$ has four possible structures

(i) $[Cr(H_2O)_6]Cl_3$ violet

(ii) $[Cr(H_2O)_5Cl]Cl_2.H_2O$ green

(iii) $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ dark green.

(iv) $[Cr(H_2O)_3Cl_3].3H_2O$ dark green.

These complexes differ from one another with respect to the number of water molecules acting as ligands. Other hydrate isomers are

$[Co(NH_3)_4(H_2O)Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl.H_2O$

(c) **Linkage isomerism**

(i) This type of isomerism arises due to presence of ambidentate ligands like

NO_2^-, CN^- and SCN^-

(ii) These ligands have two donor atoms but at a time only one atom is directly linked to the central metal atom of the complex.

(iii) Such type of isomers are distinguished by infra red (I.R.) spectroscopy.

Example. • $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$

- In NO_2^- ligand, The coordinating sites are nitrogen (i.e., NO_2^- Nitro ligand) or through oxygen (i.e. ONO Nitrito ligand)
- The nitro isomer is yellow and is stable to acids whereas nitrito isomer is red and is decomposed by acids.

(d) **Coordination isomerism**

(i) This type of isomerism is exhibited when the complex has two complex ions in it - 'cationic and anionic'.

(ii) This type of isomerism is caused by the interchange of ligands between the two complex ions of the same complex.

Example. $[Co(NH_3)_6]\ [Cr(CN)_6]$ and $[Co(NH_3)_6]\ [Cr(C_2O_4)_3]$

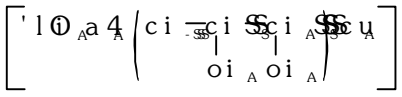
$[\ Cr(NH_3)_6]\ [Co(CN)_6]$ $[Cr(NH_3)_6]\ [Co(C_2O_4)_3]$

(e) **Ligand isomerism**

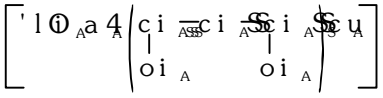
(i) Ligands with $C_3H_6(NH_2)_2$ have two different structures i.e. 1, 3-diamino propane and 1, 2-diaminopropane(propylene diamine).

(ii) Those complexes which have same molecular formula, but differ with respect to their ligands are called as **Ligand isomers**.

Example. $[Fe(H_2O)_2\ C_3H_6(NH_2)_2Cl_2]$ has two different structures

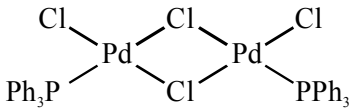


and

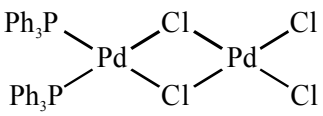


(f) **Co-ordination Position Isomerisation :**

It is shown by polynuclear complexs, due interchange of ligands between the different metal nuclei.



Example.



(g) **Polymerization Isomerism :**

This is not true isomerism because it occurs between compounds having the same empirical formula, but different molecular weights.

Example. $[Pt(NH_3)_2Cl_2]$

$[Pt(NH_3)_4]\ [PtCl_4]$

(B) Stereo isomerism

They have same molecular formula, same constitution, they differ only with respect to the spatial orientation of ligands in space around the metal ion. The two stereo isomers which are possible Geometrical and Optical.

(a) **Geometrical isomerism**

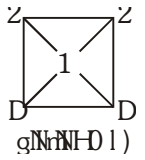
(i) The ligands occupy different positions around the central metal ion.

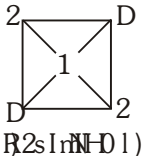
(ii) When two identical ligands are co-ordinated to the metal ion from same side then it is **cis isomer**. (Latin, cis means same).

(iii) If the two identical ligands are co-ordinated to the metal ion from opposite side then it is **trans isomer** (in Latin, trans means across).

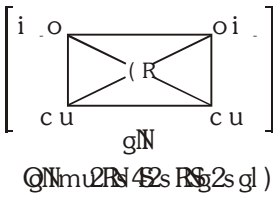
Geometrical isomers with co-ordination number = 4 (Square planar complexes)

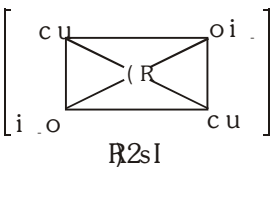
(i) Complexes with general formula, $\mathbf{Ma_2b_2}$ (where both a and b are monodentate) can have cis-and trans isomers.



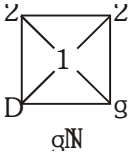


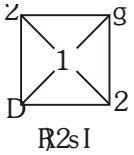
Example. **$[Pt(NH_3)_2Cl_2]$**





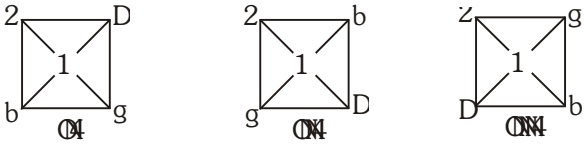
(ii) Complexes with general formula $\mathbf{Ma_2bc}$ can have cis - and trans-isomers.





Example. **$[Pt(NH_3)_2ClBr]$**

(iii) Complexes with general formula, **Mabcd** can have three isomers.

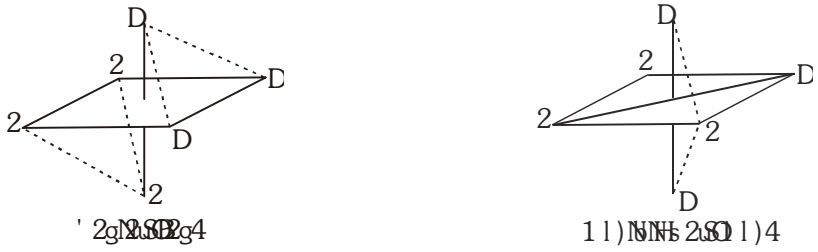


Geometrical isomers with Co-ordination number = 6

(i) Complexes with general formula **Ma_4b_2** can have cis - and trans-isomers.

Example. **$[Fe(NH_3)_4Cl_2]$**

(iii) **Facial and Meridional isomerism (Ma_3b_3)**



Other 6-Coordinated geometrical isomers are

Note :	**General formula**	**Total No. of geometrical isomers**
	Mabcdef	15
	Ma_2bcde	9
	Ma_2b_2cd	6
	$Ma_2b_2c_2$	5
	Ma_3bcd	4
	Ma_3b_2c	3
	Ma_3b_3	2
	Ma_4bc	2
	Ma_4b_2	2
	Ma_5b	Not possible
	Ma_6	Not possible

Here M = central atom a, b, c, d, e, f = Monodentate ligands

(b) **Optical isomers**

(i) Optically active complexes are those which are nonsuperimposable over the mirror image structure.

(ii) An optically active complex is one which is asymmetric in nature i.e., not divisible into two identical halves.

(iii) The complex which rotates plane polarised light to left hand side is **laevo rotatory i.e. 'ℓ' or '—'** and if the complex rotates the plane polarised light to right hand side then it is **dextro rotatory 'd' or '+'**.

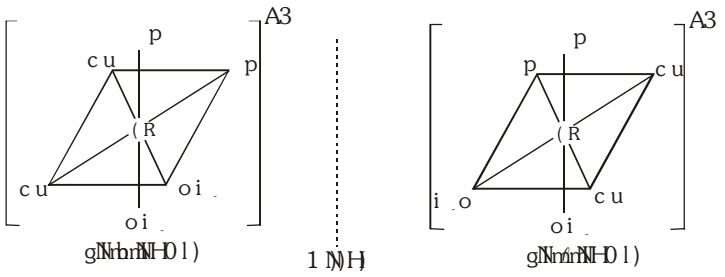
(iv) Thus complexes which have same physical and chemical properties but differ in their action towards plane polarised light are called as **optical isomers**.

(v) The 'd' and 'ℓ' isomers of a compound are called as **Enantiomers or Enantiomorphs**.

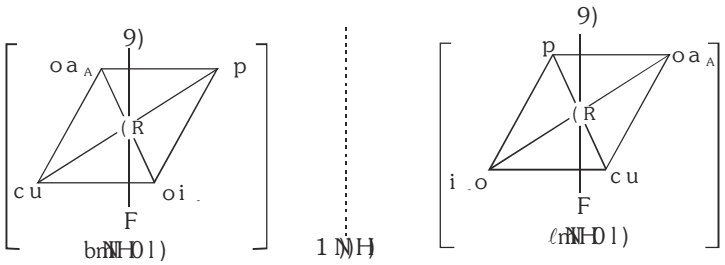
(vi) Optical isomerism is expected in tetrahedral complexes of the type Mabcd.

Optical isomers with Co-ordination number = 6

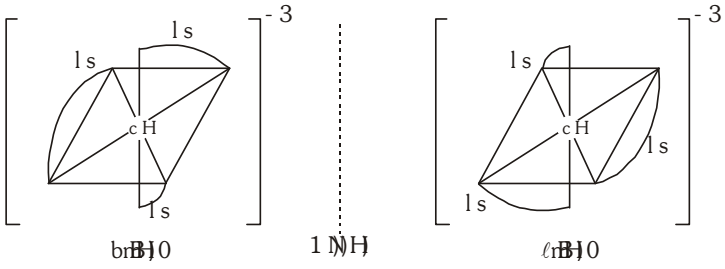
(i) $[Ma_2b_2c_2]^{n+} \rightarrow [Pt(py)_2(NH_3)_2Cl_2]^{2+}$



(ii) $[Mabcedf] \rightarrow [Pt(py)\ (NH_3)\ (NO_2)\ ClBrI]$



(iii) $[M(AA)_3]^{n+} \rightarrow [Co(en)_3]^{3+}$



NUMBER OF POSSIBLE ISOMERS FOR SPECIFIC COMPLEXES

Formula	Number of stereoisomers	Pairs of Enantiomers
$1_{2_t D_A}$	2	0
$1_{2. D.}$	2	0
$1_{2_t Dg}$	2	0
$1_{2. Dgb}$	5	1
$1_{2_A Dgbl}$	15	6
$1_{2Dgbl\ B}$	30	15
$1_{2_A D_A g_A}$	6	1
$1_{2_A D_A gb}$	8	2
$1_{2. D_A g}$	3	0
M(AA)(BC)de	10	5
M(AB)(AB)cd	11	5
M(AB)(CD)ef	20	10
$M(AB)_3$	4	2

Note : Uppercase letters represent chelating ligands and lowercase letters represent monodentate ligands.

EXERCISE # O-1

SINGLE OPTION CORRECT :

Double salt and complex compound

1. Some salts although containing two different metallic elements give test for one of them in solution. Such salts are

(A) complex salt (B) double salt (C) normal salt (D) none of these

2. Aqueous solution of $FeSO_4$ gives tests for both Fe^{2+} and SO_4^{2-} but after addition of excess of KCN, solution ceases to give test for Fe^{2+}. This is due to the formation of

(A) the double salt $FeSO_4.2KCN.6H_2O$ (B) $Fe(CN)_3$

(C) the complex ion $[Fe(CN)_6]^{4-}$ (D) the complex ion $[Fe(CN)_6]^{3-}$

Werner theory

3. Consider the following statements:

According the Werner's theory.

(a) Ligands are connected to the metal ions by covalent bonds.

(b) Secondary valencies have directional properties

(c) Secondary valencies are non-ionisable

Of these statements:

(A) a, b and c are correct (B) b and c are correct

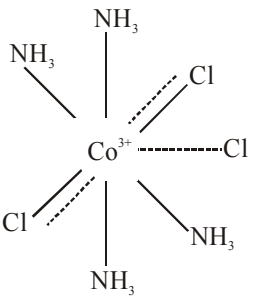
(C) a and c are correct (D) a and b are correct

4. A complex of platinum, ammonia and chloride produces four ions per molecule in the solution. The structure consistent with the observation is:

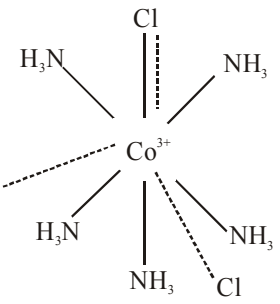
(A) $[Pt(NH_3)_4]Cl_4$ (B) $[Pt(NH_3)_2Cl_4]$ (C) $[Pt(NH_3)_5Cl]Cl_3$ (D) $[Pt(NH_3)_4Cl_2]Cl_2$

5. Which of the following Werner's complex has least electrical conductivity ?

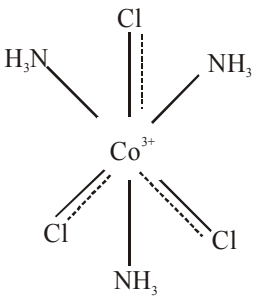
(A)



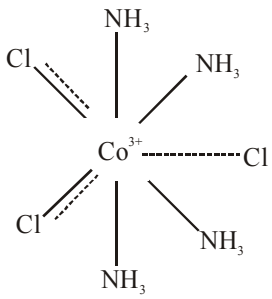
(B)



(C)



(D)



Classification of ligand

6. How many $EDTA^{-4}$ molecules are required to make an octahedral complex with a Ca^{2+} ion ?
(A) Six (B) Three (C) One (D) Two

7. π-bonding is not involved in :
(A) ferrocene (B) dibenzene chromium (C) Zeise's salt (D) Grignard reagent

8. Which of the following is not considered as an organometallic compound ?
(A) Ferrocene (B) Cis-platin (C) Ziese's salt (D) Grignard reagent

9. Diethylene triamine is:
(A) Chelating agent (B) Polydentate ligand
(C) Tridentate ligand (D) All of these

10. Which of the following species is not expected to be a ligand
(A) NO^+ (B) NH_4^+ (C) $NH_2-NH_3^+$ (D) CO

11. The disodium salt of ethylene diamine tetraacetic acid can be used to estimate the following ion(s) in the aqueous solution
(A) Mg^{2+} ion (B) Ca^{2+} ion (C) Na^+ ion (D) both Mg^{2+} and Ca^{2+}

12. Which of the following ligand does not act as bidentate ligand
(A) dipy (B) dien (C) gly^- (D) dmg^-

Synergic bonding

13. Which of the following order is correct for the IR vibrational frequency of CO.
(A) $[Fe(CO)_4]^{2-} < [Co(CO)_4]^- < [Ni(CO)_4]$ (B) $[Fe(CO)_4]^{2-} > [Co(CO)_4]^- > [Ni(CO)_4]$
(C) $[Fe(CO)_4]^{2-} > [Co(CO)_4]^- < [Ni(CO)_4]$ (D) $[Fe(CO)_4]^{2-} < [Co(CO)_4]^- > [Ni(CO)_4]$

14. In the isoelectronic series of metal carbonyl, the C–O bond strength is expected to increase in the order.
(A) $[Mn(CO)_6]^+ < [Cr(CO)_6] < [V(CO)_6]^-$ (B) $[V(CO)_6]^- < [Cr(CO)_6] < [Mn(CO)_6]^+$
(C) $[V(CO)_6]^- < [Mn(CO)_6]^+ < [Cr(CO)_6]$ (D) $[Cr(CO)_6] < [Mn(CO)_6]^+ < [V(CO)_6]^-$

15. Which of the following has higher stretching frequency for C–O bond -
(A) $[Ni(CO)_3PF_3]$ (B) $[Ni(CO)_3(PMe_3)]$
(C) both have equal stretching frequency (D) None of these

16. Which of the following has higher multiple bond character in M–C bond -
(A) $[Ni(CO)_4]$
(B) $[Co(CO)_4]^-$
(C) $[Fe(CO)_4]^{2-}$
(D) (B) and (C) both have equal multiple bond character in M–C bond

17. The V–C distance in $V(CO)_6$ and $[V(CO)_6]^-$ are respectively (in pm)-
(A) 200, 200 (B) 193, 200 (C) 200, 193 (D) 193, 193

Co-ordination number and E.A.N.

18. Among the following complexes which can act as oxidising agent.

(A) $[Mn(CO)_6]$ (B) $[Mn(CO)_6]^+$ (C) $[Mn(CO)_5]^-$ (D) $[V(CO)_6]$

19. Which of the following statement is correct regarding the compound " $[(CO)_3Fe(CO)_3Fe(CO)_3]$".

(A) The d_{C-O} (bridging) is greater than d_{C-O} (terminal)

(B) The bond order of bridging C – O bond is greater than that of terminal C – O bond

(C) The E.A.N. value of each Fe-atom is 35

(D) The oxidation state of Fe in this complex is (–I)

20. How many π electrons are donated by $C_5H_5^-$ ligand -

(A) 2 (B) 4 (C) 5 (D) 6

21. Effective atomic number of $Co(CO)_4$ is 35, hence it is less stable. It attains stability by

(A) Oxidation of Co (B) Reduction of Co

(C) Dimerization (D) Both (B) & (C)

22. In the complex $Fe(CO)_x$, the value of x is:

(A) 3 (B) 4 (C) 5 (D) 6

23. The EAN of platinum in potassium hexachloroplatinate (IV) is:

(A) 46 (B) 86 (C) 36 (D) 84

24. The EAN of metal atoms in $Fe(CO)_2(NO)_2$ and $Co_2(CO)_8$ respectively are

(A) 34, 35 (B) 34, 36 (C) 36, 36 (D) 36, 35

Naming of complex compound

25. The IUPAC name for the coordination compound $Ba[BrF_4]_2$ is

(A) Barium tetrafluorobromate (V) (B) Barium tetrafluorobromate (III)

(C) Barium bis (tetrafluorobromate) (III) (D) none of these

26. The number of ions formed, when bis (ethane-1,2-diamine) copper (II) sulphate is dissolved in water will be

(A) 1 (B) 2 (C) 3 (D) 4

27. The IUPAC name of the Wilkinson's catalyst [Rh Cl (P $Ph_3)_3$] is

(A) Chloridotris(triphenylphosphine)rhodium(I)

(B) Chloridotris(triphenylphosphine)rhodium(IV)

(C) Chloridotris(triphenylphosphine)rhodium(0)

(D) Chloridotris(triphenylphosphine)rhodium(VI)

28. The formula for the compound tris (ethane-1, 2-diamine)cobalt (III) sulphate is

(A) $[Co(en)_3]SO_4$ (B) $[Co(SO)_4(en)_3]$

(C) $[Co(en)_3](SO_4)_2$ (D) $[Co(en)_3]_2(SO_4)_3$

Structural isomerism

29. Which of the following statement is **INCORRECT** regarding the following compound

$[Pt(NH_3)_4]\,[PtCl_4]$

(A) It is the polymerisation isomer of $[Pt(NH_3)_3Cl_3]$

(B) E.A.N. of cationic part is equal to that of anionic part

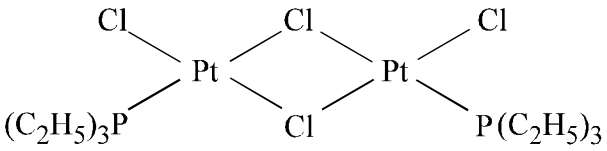
(C) It is the co-ordination isomer of $[Pt(NH_3)_3Cl]\,[Pt(NH_3)Cl_3]$

(D) Synergic bonding is not involved in the complex

30. The type of isomerism present in pentaamminenitrochromium (III) chloride is :

(A) optical (B) linkage (C) hydrate (D) polymerisation

31. The complexes given below show:



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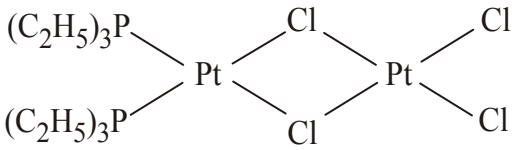


(A) Optical isomerism (B) Co-ordination isomerism

(C) Geometrical isomerism (D) Co-ordination position isomerism

32. Which of the following complex shows ionization isomerism

(A) $[Cr(NH_3)_6]Cl_3$ (B) $[Cr(en)_2]Cl_2$

(C) $[Cr(en)_3]Cl_3$ (D) $[CoBr(NH_3)_5]SO_4$

33. Find the name of the hydrate isomer of $CrCl_3.6H_2O$, which is having lowest electrical conductivity excluding zero value of conductivity.

(A) Hexaaquachromium(III) chloride

(B) Tetraaquadichloridochromium(III) chloride dihydrate

(C) Pentaaquachloridochromium(III) chloride monohydrate

(D) Triaquatrichloridochromium(III) chloride trihydrate

Stereoisomerism

34. Which of the following complex shows optical isomerism -

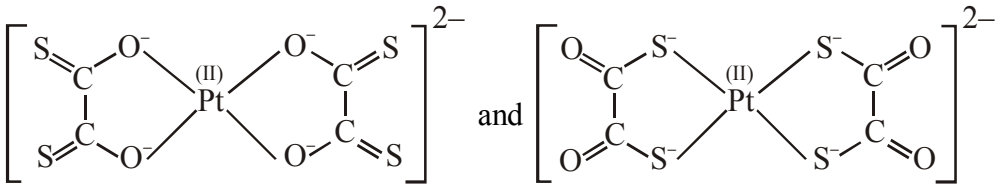
(A) $[Cd(CN)_4]^{2-}$ (B) $[Cr(H_2O)_3Cl_3].3H_2O$

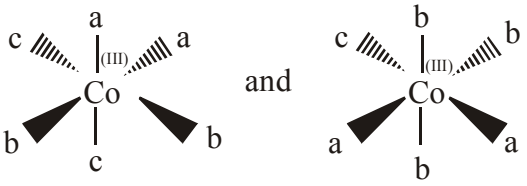
(C) $[Zn(gly)_2]^o$ (D) $[Ni(dmg)_2]^o$

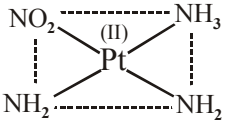
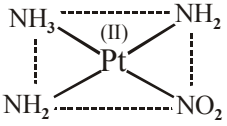
35. How many coordination isomers of $[Pt(NH_3)_4][PtCl_4]$ show geometrical isomerism.

(A) All (B) One (C) Two (D) None

36. Identify the pair of complex which are stereoisomer of each other -

(A)  and

(B)  and

(C)  & 

(D) All of the above

37. Find complex which have maximum number of stereoisomers -

(A) $[Ma_3b_3]$ (B) $[Ma_3b_2c]$ (C) $[Ma_2b_2c_2]$ (D) $[M(AA)a_2b_2]$

38. In which of the following pairs both the complexes show optical isomerism ?

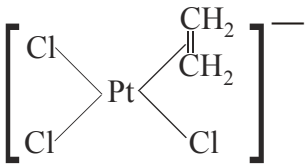
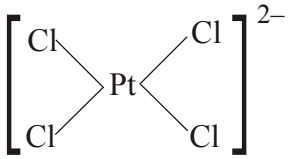
(A) cis-$[Cr(C_2O_4)_2Cl_2]^{3-}$, trans-$[Co(NH_3)_4Cl_2]$

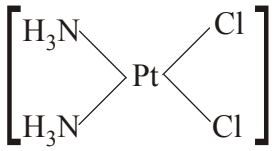
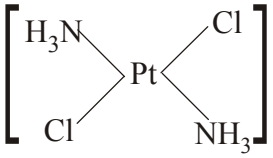
(B) $[Co(en)_3]Cl_3$, cis-$[Co(en)_2Cl_2]Cl$

(C) $[PtCl(dien)]Cl$, $[NiCl_2Br_2]^{2-}$

(D) $[Co(NO_3)_3(NH_3)_3]$, cis-$[Pt(en)_2Cl_2]$

39. Which of the following is considered to be an anticancer species ?

(A)  (B) 

(C)  (D) 

40. Which of the following can exhibit geometrical isomerism ?

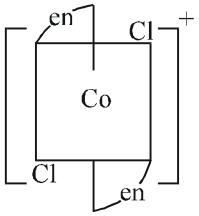
(A) $[MnBr_4]^{2-}$ (B) $[Pt(NH_3)_3Cl]^{+}$

(C) $[PtCl_2(P(C_2H_5)_3)_2]$ (D) $[Fe(H_2O)_5NOS]^{2+}$

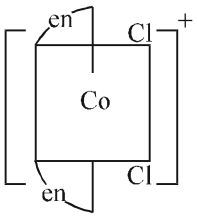
41. The oxidation state of Mo in its oxo-complex species $[Mo_2O_4(C_2H_4)_2(H_2O)_2]^{2-}$ is:

(A) +2 (B) +3 (C) +4 (D) +5

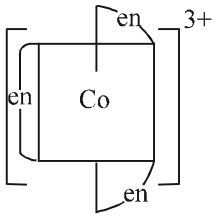
42. Which of the following ions are optically active?



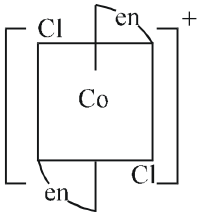
(I)



(II)



(III)

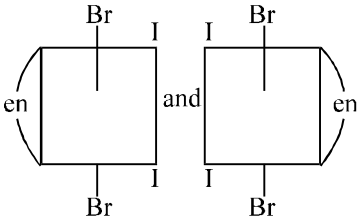


(IV)

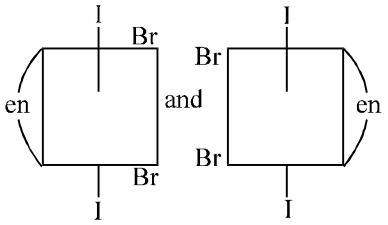
(A) I only (B) II only (C) II and III (D) IV only

43. The complex ion has two optical isomers. Their **CORRECT** configurations are:

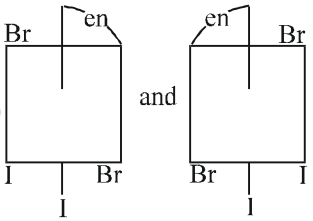
(A)



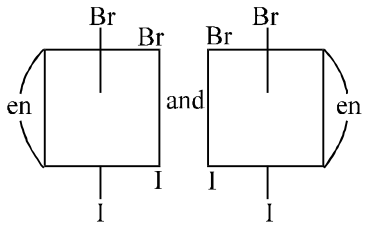
(B)



(C)



(D)



V.B.T/CFT

44. Which of the following complex is coloured and diamagnetic -

(A) MnO_4^{2-} (B) $[Ni(H_2O)_6]^{2+}$ (C) $[CrCl_6]^{3-}$ (D) CrO_4^{2-}

45. What is the hybridisation of Fe in $[Fe(CO)_4]^{-2}$

(A) d^2sp^3 (B) sp^3d^2 (C) sp^3d (D) sp^3

46. One unknown complex has the spin only magnetic moment is of 1.73 BM. As per the C. F. T., complexe is.

(A) d^7, Oh-field, with Srong Feild Legand (B) d^9, sq.planar-field, with Srong Feild Legand

(C) d^9, Td,field with Weak Feild Legand (D) All of these

47. Identify tetrahedral species which has maximum magnetic moment value :

(A) $[CuCl_4]^{2-}$ (B) $[CoCl_4]^{2-}$ (C) $[FeCl_4]^{2-}$ (D) $[AlCl_4]^-$

48. In the co-ordination compound $Na_4[Fe(CN)_5NOS]$ oxidation state of Fe is -

(A) +1 (B) +2 (C) +3 (D) +4

49. Which one of the following complex is an outer orbital complex -

(A) $[Ni(H_2O)_6]^{+2}$ (B) $[Fe(H_2O)_5NO]SO_4$

(C) $[Fe(NH_3)_6]^{+2}$ (D) All of these

50. Which of the following is diamagnetic and sp^3 hybridised -

(A) $[NiCl_4]^{2-}$ (B) $[Ni(CN)_4]^{4-}$ (C) $[Ni(CN)_4]^{2-}$ (D) $[NiCl_2(PPh_3)_2]$

51. $[Cr(H_2O)_6]Cl_3$ (atomic number of Cr = 24) has a magnetic moment of 3.83 B.M. The **CORRECT** distribution of 3d electrons in the chromium present in the complex is:

(A) $3d^1_{xy}$, $3d^1_{yz}$, $3d^1_{zx}$ (B) $3d^1_{xy}$, $3d^1_{yz}$, $3d^1_{z^2}$

(C) $3d^1_{(x^2-y^2)}, 3d^1_{z^2}, 3d^1_{xz}$ (D) $3d^1_{xy}, 3d^1_{(x^2-y^2)}, 3d^1_{yz}$

52. $[Fe(H_2O)_6]^{+2}$ has Crystal Field Splitting Energy value 10,400 cm^{-1} and pairing energy value 17,600 cm^{-1} then it is :

(A) Low spin complex (B) Paramagnetic in nature

(C) Diamagnetic in nature (D) None of these

53. In which of the following coordination entities, the magnitude of Δ_0 [CFSE in octahedral field] will be maximum? :

(A) $[Co(CN)_6]^{3-}$ (B) $[Co(C_2O_4)_3]^{3-}$

(C) $[Co(H_2O)_6]^{3+}$ (D) $[Co(NH_3)_6]^{3+}$

54. The number of unpaired electrons calculated in $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$ are :

(A) 4 and 4 (B) 0 and 2 (C) 2 and 4 (D) 0 and 4

55. An ion M^{2+}, forms the complexes $[M(H_2O)_6]^{2+}$, $[M(en)_3]^{2+}$ and $[MBr_6]^{4-}$, match the complex with the appropriate colour.

(A) Green, blue and red (B) Blue, red and green

(C) Green, red and blue (D) Red, blue and green

56. Formula of ferrocene is:

(A) $[Fe(CN)_6]^{4-}$ (B) $[Fe(CN)_6]^{3+}$ (C) $[Fe(CO)_5]$ (D) $[Fe(C_5H_5)_2]$

57. $Ni(CO)_4$ and $[Ni(NH_3)_4]^{2+}$ do not differ in

(A) magnetic moment (B) oxidation number of Ni

(C) geometry (D) EAN

58. A complex of certain metal has the magnetic moment of 4.91 BM whereas another complex of the same metal with same oxidation state has zero magnetic moment. The metal ion could be

(A) Co^{2+} (B) Mn^{2+} (C) Fe^{2+} (D) Fe^{3+}

59. The tetrahedral $[CoI_4]^{2-}$ and square planar $[PdBr_4]^{2-}$ complex ions are respectively

(A) low spin, high spin (B) high spin, low spin

(C) both low spin (D) both high spin

60. Which one of the following species does not represent cationic species of vanadium formed in aqueous solution

(A) VO_2^+ (B) VO^{2+} (C) $[V(H_2O)_6]^{3+}$ (D) VO_2^{2+}

61. On treatment of $[Ni(NH_3)_4]^{2+}$ with concentrated HCl, two compounds I and II having the same formula, $[NiCl_2(NH_3)_2]$ are obtained, I can be converted into II by boiling with dilute HCl. A solution of I reacts with oxalic acid to form $[Ni(C_2O_4)(NH_3)_2]$ wheras II does not react. Point out the correct statement of the following

(A) I cis, II trans; both tetrahedral (B) I cis, II trans; both square planar

(C) I trans, II cis; both tetrahedral (D) I trans, II cis; both square planar

62. Among the following, the compound that is both paramagnetic and coloured is

(A) $K_2Cr_2O_7$ (B) $(NH_4)_2[TiCl_6]$ (C) $VOSO_4$ (D) $K_3[Cu(CN)_4]$

63. The magnetic moment of $[NiX_4]^{2-}$ ion is found to be zero. Then the metal of the complex ion is (X = monodentate anionic ligand).

(A) sp^3 hybridised (B) spd^2 hybridised (C) dsp^2 hybridised (D) d^2sp hybridised

64. For which of the following types of d^n configuration, the number of unpaired electrons in octahedral complexes remains same irrespective of the ligand field strength.

(A) d^3 (B) d^4 (C) d^5 (D) d^6

65. Which of the follwoing electronic arrangement gives the highest value of the magnetic moment?

(A) d^6, strong field (B) d^7, high spin (C) d^4, weak field (D) d^2, strong field

66. Select appropriate ligand for given complex

$[\overset{III}{Co}(.....)_6]^{\pm x}$; $\mu = 0$ BM

(A) $C_2O_4^{2-}$ (B) en (C) H_2O (D) F^-

67. According to C.F.T. , ligands are treated as -

(A) Point charges (B) Lewis acids (C) Proton donor (D) All of the above

68. Which of the following is correct electronic configuration of 3d orbital in excited state of central metal ion, when $[Ti(H_2O)_6]^{3+}$ absorbed yellow-green light.

(A) 3d | | | | 1 | | (B) t_{2g}^1, e_g^0

(C) t_{2g}^1, e_g^1 (D) t_{2g}^0, e_g^1

69. If $\lambda_{absorbed}$ for d-d transition is in order $[Ti(X)_6]^{3+} > [Ti(Y)_6]^{3+} > [Ti(Z)_6]^{3+}$.

Select correct order of strength of ligands (X, Y, Z are monodentate ligand)-

(A) Z > Y > X (B) X > Y > Z

(C) Z > X > Y (D) Not predictable

EXERCISE # O-2

MORE THAN ONE MAY BE CORRECT

1. Which of the following exhibit geometrical isomerism (M stands for a metal, and a and b are achiral ligands)?

(A) Ma_2b_2 (Sq. Pl.) (B) Ma_4b_2 (C) Ma_5b (D) Ma_6

2. Which of the following statement(s) is (are) **CORRECT** ?

(A) The oxidation state of iron in sodium nitroprusside $Na_2[Fe(CN)_5(NO)]$ is +II.

(B) $[Ag(CN)_2]^-$ is linear in shape.

(C) In $[Fe(H_2O)_6]^{3+}$, Fe is d^2sp^3 hybridized.

(D) In $Ni(CO)_4$, the oxidation state of Ni is zero.

3. Which of the following compound(s) show(s) optical isomerism.

(A) $[Pt(bn)_2]^{2+}$ (B) $[CrCl_2(en)_2]^+$ (C) $[Co(en)_3]\,[CoF_6]$ (D) $[Zn(gly)_2]$

4. Select **INCORRECT** statement(s) for $[Cu(CN)_4]^{3-}$, $[Cd(CN)_4]^{2-}$ and $[Cu(NH_3)_4]^{2+}$ complex ion.

(A) Both $[Cd(CN)_4]^{2-}$ and $[Cu(NH_3)_4]^{2+}$ have square planar geometry

(B) $[Cu(CN)_4]^{3-}$ and $[Cu(NH_3)_4]^{2+}$ have equal no. of unpaired electron

(C) $[Cu(CN)_4]^{3-}$ and $[Cd(CN)_4]^{2-}$ can be separated from the mixture on passing H_2S gas.

(D) All the three complexes have magnetic moment equal to zero.

5. Which of the following will have two stereoisomeric forms?

(A) $[Cr(NO_3)_3(NH_3)_3]$ (B) $K_3[Fe(C_2O_4)_3]$

(C) $[CoCl_2(en)_2]^+$ (D) $[CoBrCl(Ox)_2]^{3-}$

6. Which is / are **NOT** correctly matched.

	Complex compounds	**IUPAC name**
(A)	$K[CrF_4O]$	Potassium tetrafluoridooxidochromate(V)
(B)	$Na[BH(OCH_3)_3]$	Sodium hydridotrimethoxyborate(III)
(C)	$[Be(CH_3–CO–CH_2–CO–C_6H_5)_2]°$	Bis(benzoylacetonato)beryllium(III)
(D)	$H[AuCl_4]$	Hydrogen tetrachloroaurate(III)

7. Which of the following statement(s) is/are **INCORRECT**

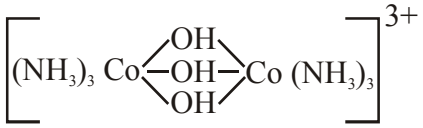
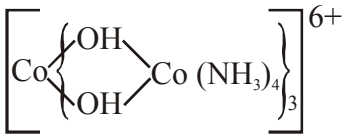
(A) In $[CoBrCl(en)_2]^+$ geometrical isomerism exists, while optical isomerism does not exist

(B) Potassium aquadicyanidosuperoxidoperoxidochromate(III) is IUPAC name for $K_2[Cr(CN)_2O_2(O_2)(H_2O)]$

(C) There are 3 geometrical isomers and 15 stereoisomers possible for $[Pt(NO_2)(NH_3)(NH_2OH)(py)]^+$ and [PtBr C*l* I $(NO_2)(NH_3)(py)$] respectively

(D) cis and trans forms are not diastereomers of each other

8. Which of the following complexes are polymerisation isomers :

(A)  and 

(B) $[Pt(NH_3)_4]\,[PtCl_4]$ and $[Pt(NH_3)_4]\,[Pt(NH_3)Cl_3]_2$

(C) $[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_3Cl]_2\,[PtCl_4]$

(D) $[Pt(NH_3)_2Cl_4]$ and $[Pt(NH_3)_2Cl_2]$

9. Which of the following is **CORRECT** about

Tetraamminedithiocyanato-Scobalt(III) tris(oxalato)cobaltate(III)

(A) formula of the complex is $[Co(SCN)_2(NH_3)_4][Co(ox)_3]$

(B) It is a chelating complex and show linkage isomerism.

(C) It shows optical isomerism.

(D) It shows geometrical isomerism.

10. Which is **CORRECT** statement(s)?

(A) $[Ag(NH_3)_2]^+$ is linear with sp hybridised Ag^+ ion

(B) $NiCl_4^{2-}$, VO_4^{3-} and MnO_4^- have tetrahedral geometry

(C) $[Cu(NH_3)_4]^{2+}$, $[Pt(NH_3)_4]^{2+}$ & $[Ni(CN)_4]^{2-}$ have dsp^2 hybridisation of the metal ion

(D) $Fe(CO)_5$ has trigonal bipyramidal structure with $d_{z^2}sp^3$ hybridised iron.

11. In which of the following complex(s) spin only magnetic moment is independent , from the nature of ligand. (L = monodented ligand) -

(A) $[\overset{II}{N}iL_4]$ (B) $[\overset{II}{N}iL_6]$ (C) $[\overset{III}{F}eL_6]$ (D) $[\overset{III}{C}rL_6]$

12. Which of the following compound(s) can show optical isomerism ?

(A) $[PtCl_4]^{2-}$ (B) $[PtCl_2(NH_3)_2]$ (C) $[Fe(EDTA)]^-$ (D) $[Fe(en)_3]^{3+}$

13. Which of the following compounds are resolvable into d or ℓ-forms?

(A) $[ZnCl_2(en)]$ (B) $[Be(acac)_2]$ (C) $[Co(gly)_3]$ (D) $[Cr(C_2O_4)_3]^{3-}$

14. Which of the following ion is/are diamagnetic and non planar ?

(A) $[Ni(CN)_4]^{2-}$ (B) MnO_4^- (C) $[Cu(NH_3)_4]^{2+}$ (D) CrO_4^{2-}

EXERCISE # S-1

INTEGER TYPE

1. Find number of ligands which is / are stronger ligand as compared to NH_3

NO_2^-, H_2O, NO_3^-, F^-, $C_2O_4^{2-}$, en, Cl^-, $\overline{C}N$

2. If crystal field stablization energy of $[ML_6]^{+n}$ is $-0.8\ \Delta_O$.

Find minimum number of electrons in t_{2g} orbitals of metal ion ?

3. Find number of Co–N linkage in,

Pentaamminecobalt(III)–μ–amidodiamminetriaquacobalt(III) chloride.

4. Find the EAN value of central atom of $[Fe(\pi\text{–}C_4H_4)\ (CO)_3]$

5. Find the maximum number of atoms lying in one plane for $[Cr(CN)_6]^{3-}$

6. Select complex in which metal–carbon linkage(s) is / are present :

$\left[\overset{III}{Fe}(EDTA)\right]^-$, $K[PtCl_3(\pi\text{–}C_2H_4)]$, $[Cr(acac)_3]^o$, $[Fe(CO)_5]$, $[Co(C_2H_5O)_6]^{3-}$, $[Ni(dmg)_2]$

7. Find out the total number of geometrical isomers of $[Co(H_2O)_3Cl_3]$.

8. Find the value of E.A.N of $[Pd(CO)_4]^{+2}$ (atomic number = 46) :

9. A co-ordination compound have magnetic moment 5.92 B.M. Find out the number of unpaired electron(s) in the compound.

10. Find the number of optically active isomers for $[Pd(en)_2(NH_3)(H_2O)]^{4+}$ cation.

EXERCISE # S-2

MATCH THE COLUMN :

1. Match the complexes in column-I with the EAN of central atom in column-II:

	Column-I		**Column-II**
(A)	$[Fe(CO)_4]^{2-}$	(P)	34
(B)	$[Co(NH_3)_5Cl]Cl_2$	(Q)	35
(C)	$K_2[Ni(CN)_4]$	(R)	36
(D)	$[Cu(NH_3)_4]^{2+}$	(S)	37

2.

	Column - I		**Column -II**
(A)	$Na_2\ [Fe(CN)_5\ NO]$	(P)	$\mu = 0$ B.M.
(B)	$[Fe(H_2O)_5\ NO]\ SO_4$	(Q)	octahedral
(C)	$[Ag(CN)_2]^-$	(R)	$\mu = \sqrt{15}$ B.M.
(D)	$K_4[Fe(CN)_6]$	(S)	NO^+ ligand

3. Match the complexes in column I with their stereoproperties is column II

	Column I		**Column II**
(A)	$[CoCl_3(NH_3)_3]$	(P)	Has a facial isomer
(B)	$[Cr\ (ox)_3]^{3-}$	(Q)	Cis form is optically active
(C)	$[CrCl_2(ox)_2]$	(R)	Trans form is optically inactive
(D)	$[RhCl_3(Py)_3]$	(S)	Has a meridional form
		(T)	Two optically active isomer

4. Match each coordination compound in List-I with co-ordination number of central metal/ion from List-II and select the correct answer using the code given below the lists.

List-I	**List-II**
(P) $[Co(en)_3]^{3+}$	(1) 6
(Q) $[Ca(EDTA)]^{2-}$	(2) 4
(R) $[Ni(CO)_4]$	(3) 2
(S) $[Ag(NH_3)_2]Cl$	(4) 5

Code :

	P	**Q**	**R**	**S**
(A)	2	1	2	3
(B)	1	1	2	3
(C)	1	4	2	3
(D)	1	1	3	2

5. Match the List-I with List-II :

List-I	**List-II**
(P) Ferrocene	(1) Iron present
(Q) $Mn_2(CO)_{10}$	(2) Cobalt
(R) Vitamine B_{12}	(3) Metal-Metal bonding
(S) Haemoglobin	(4) Sandwich structure

Code :

	P	**Q**	**R**	**S**
(A)	4	3	1	2
(B)	1	3	1	2
(C)	1,4	3	2	1
(D)	1	3	4	2

6. Match the List-I with List-II :

List-I	**List-II**
(P) $EDTA^{4-}$	(1) N-donor atom
(Q) en	(2) Chelate ligand with same donor site
(R) gly^-	(3) Bidentate with different donor atom
(S) amide	(4) Hexadentate

Code :

	P	**Q**	**R**	**S**
(A)	4	2	1	3
(B)	2	1	3	4
(C)	4	1	2	3
(D)	4	2	3	1

Assertion Reason :

7. **Statement-1**: Complexes containing three bidentate groups such as $[Cr(ox)_3]^{3-}$ and $[Co(en)_3]^{3+}$ do not show optical activity.

Statement-2: Octahedral complex, $[Co(NH_3)_4Cl_2]Cl$ shows geometrical isomerism.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

8. **Statement-1**: After splitting of d-orbitals during complex formation, the orbitals form two sets of orbitals t_{2g} and e_g in an octahedral field.

Statement-2: Splitting of d-orbitals occur only in the case of strong field ligands such as CN^-.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

9. **Statement-1**: $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless.

Statement-2: d–d transition is not possible in $[Sc(H_2O)_6]^{3+}$ because no d-electron is present while possible for Ti^{3+} having d^1 system.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

Comprehension (10 to 12)

Ligands are neutral or ionic species capable of donating at least one electron pair to central metal. Hence ligands can be of different denticities.

10. For a given metal M^{3+} coordination number is six, then for which set of ligands, complex will be most stable-

(A) $6H_2O$ (B) $6F^-$ (C) $EDTA^{4-}$ (D) $2H_2O$ and $2C_2O_4^{2-}$

11. $[Mn(CO)_5]$ can attain more stability by :

(A) Oxidation of itself (B) Reduction of itself

(C) Dimerization (D) Both (B) and (C)

12. The metal cation that has least tendency to accept electron pair from NH_3 is

(A) Fe^{3+} (B) Rh^{3+} (C) Zn^{2+} (D) Ba^{++}

Comprehension (13 to 15)

Complex compounds are molecular compounds which retain their identities even when dissolved in water. They do not give all the simple ions in solution but instead furnish complex ions with complicated structures. The complex compounds are often called coordination compounds because certain groups called ligands are attached to the central metal ion by coordinate or dative bonds. Coordination compounds exhibit isomerism, both structural and stereoisomerism. The structure, magnetic property, colour and electrical properties of complexes are explained by various theories.

13. Arrange the following compounds in order of their Molar conductance:

(I) $K[Co(NO_2)_4(NH_3)_2]$ (II) $[Cr(ONO)_3(NH_3)_3]$

(III) $[Cr(NO_2)(NH_3)_5]_3[Co(NO_2)_6]_2$ (IV) $Mg[Cr(NO_2)_5(NH_3)]$

(A) II < I < IV < III (B) I < II < III < IV

(C) II < I < III < IV (D) IV < III < II < I

14. The oxidation number and coordination number of chromium in the following complex is $[Cr(C_2O_4)_2(NH_3)_2]^{1-}$

(A) O.N. = + 4, C.N. = 4 (B) O.N. = +3, C.N. = 4

(C) O.N. = – 1, C.N. = 4 (D) O.N. = + 3, C.N. = 6

15. In which of the following pairs, both the complexes have the same geometry but different hybridisation

(A) $[NiCl_4]^{2-}$, $[Ni(CN)_4]^{2-}$ (B) $[CoF_6]^{3-}$, $[Co(NH_3)_6]^{3+}$

(C) $[Ni(CO)_4]$, $[Ni(CN)_4]^{2-}$ (D) $[Cu(NH_3)_4]^{2+}$, $[Ni(NH_3)_6]^{2+}$

Matching list type 1 × 3Q. (Three list type Question)

The following column I, II, III represent the different type of observations based on CFT in complex compounds.

Answer the questions that follow

Column-I - Crystal field stablization energy (CFSE) (neglecting PE in all cases)

Column-II - Electronic configuration

Column-III - Type of complex

Column - I CFSE (neglecting PE in all cases	**Column - II** Electronic Configuration	**Column - III** Type of Complex
(I) $-0.4\ \Delta_O$	(i) t_{2g}^5, e_g^0	(P) High spin & Paramagnetic
(II) $-2.0\ \Delta_O$	(ii) t_{2g}^4, e_g^0	(Q) Low spin & Paramagnetic
(III) $-2.4\ \Delta_O$	(iii) t_{2g}^6, e_g^0	(R) High spin & Diamagnetic
(IV) $-1.2\ \Delta_O$	(iv) t_{2g}^4, e_g^2	(S) Low spin & Diamagnetic

16. For sodium nitroprusside complex the only **CORRECT** combination is

(A) (III), (iv), (Q) (B) (III), (iii), (S) (C) (III), (iii), (R) (D) (II), (iii), (Q)

17. For $[Co(H_2O)_3F_3]$ complex the only **CORRECT** combination is.

(A) (I), (iv), (Q) (B) (II), (iv), (S) (C) (III), (ii), (R) (D) (I), (iv), (P)

18. For $[Mn(CN)_6]^{4-}$ complex the only **CORRECT** combination is.

(A) (IV), (i), (S) (B) (II), (i), (R) (C) (I), (i), (S) (D) (II), (i), (Q)

EXERCISE # JEE-MAIN

1. In $[Cr(C_2O_4)_3]^{3-}$, the isomerism shown is - **[AIEEE-2002]**

(1) Ligand (2) Optical (3) Geometrical (4) Ionization

2. In the complexes $[Fe(H_2O)_6]^{3+}$, $[Fe(SCN)_6]^{3-}$, $[Fe(C_2O_4)_3]^{3-}$ and $[FeCl_6]^{3-}$, more stability is shown by - **[AIEEE-2002]**

(1) $[Fe(H_2O)_6]^{3+}$ (2) $[Fe(SCN)_6]^{-3}$ (3) $[Fe(C_2O_4)_3]^{3-}$ (4) $[FeCl_6]^{3-}$

3. One mole of the complex compound $Co(NH_3)_5Cl_3$, gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of $AgNO_3$ solution to yield two moles of AgCl(s). The structure of the complex is - **[AIEEE-2003]**

(1) $[Co(NH_3)_3Cl_3].2NH_3$ (2) $[Co(NH_3)_4Cl_2]Cl.NH_3$

(3) $[Co(NH_3)_4Cl]Cl_2.NH_3$ (4) $[Co(NH_3)_5Cl]Cl_2$

4. In the coordination compound $K_4[Ni(CN)_4]$, the oxidation state of nickel is – **[AIEEE-2003]**

(1) 0 (2) +1 (3) +2 (4) –1

5. The number of 3d-electrons remained in Fe^{2+} (At.no. of Fe = 26) ion is – **[AIEEE-2003]**

(1) 4 (2) 5 (3) 6 (4) 3

6. Ammonia forms the complex ion $[Cu(NH_3)_4]^{2+}$ with copper ions in alkaline solutions but not in acidic solution. What is the reason for it :- **[AIEEE-2003]**

(1) In acidic solutions hydration protects copper ions

(2) In acidic solutions protons coordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available

(3) In alkaline solutions insoluble $Cu(OH)_2$ is precipitated which is soluble in excess of any alkali

(4) Copper hydroxide is an amphoteric substance

7. Among the properties (a) reducing (b) oxidising (c) complexing, the set of properties shown by CN^- ion towards metal species is :- **[AIEEE-2004]**

(1) c, a (2) b, c (3) a, b (4) a, b, c

8. The coordination number of a central metal atom in a complex is determined by :- **[AIEEE–2004]**

(1) The number of ligands around a metal ion bonded by sigma and pi-bonds both

(2) The number of ligands around a metal ion bonded by pi-bonds

(3) The number of ligands around a metal ion bonded by sigma bonds

(4) The number of only anionic ligands bonded to the metal ion

9. Which one of the following complexes is an outer orbital complex :- **[AIEEE–2004]**

(1) $[Co(NH_3)_6]^{3+}$ (2) $[Mn(CN)_6]^{4-}$

(3) $[Fe(CN)_6]^{4-}$ (4) $[Ni(NH_3)_6]^{2+}$

(Atomic nos.:Mn=25 ; Fe=26 ; Co=27 ; Ni = 28)

10. Coordination compounds have great importance in biological systems. In this contect which of the following statements is **INCORRECT** ? **[AIEEE–2004]**

(1) Cyanocobalamin is vitamin B_{12} and contains cobalt

(2) Haemoglobin is the red pigment of blood and contains iron

(3) Chlorophylls are green pigments in plants and contain calcium

(4) Carboxypeptidase - A is an enzyme and contains zinc

11. The **CORRECT** order of magnetic moments (spin only values in B.M.) among is :- **[AIEEE–2004]**

(1) $[Fe(CN)_6]^{4-} > [MnCl_4]^{2-} > [CoCl_4]^{2-}$ (2) $[MnCl_4]^{2-} > [Fe(CN)_6]^{4-} > [CoCl_4]^{2-}$

(3) $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [Fe(CN)_6]^{4-}$ (4) $[Fe(CN)_6]^{4-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$

(Atomic nos. : Mn = 25, Fe = 26, Co = 27)

12. For octahedral complex, the value of the 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The **CORRECT** one is **[AIEEE–2005]**

(1) d^4 (in strong ligand field) (2) d^4 (in weak ligand field)

(3) d^3 (in weak as well as in strong field) (4) d^5 (in strong ligand field)

13. The IUPAC name for the complex $[Co(NO_2)(NH_3)_5]Cl_2$ is - **[AIEEE–2006]**

(1) pentaammine nitrito-N- cobalt (II) chloride

(2) pentaammine nitrito-N- cobalt (III) chloride

(3) nitrito-N- pentaamminecobalt (III) chloride

(4) nitrito-N- pentaamminecobalt (II) chloride

14. Nickel (Z=28) combines with a uninegative monodentate ligand X^- to form a paramagnetic complex $[NiX_4]^{2-}$. The number of unpaired electrons in the nickel and geometry of this complex ion are, respectively. **[AIEEE–2006]**

(1) one, square planar (2) two, square planar (3) one, tetrahedral (4) two, tetrahedral

15. In $Fe(CO)_5$, the Fe–C bond possesses **[AIEEE–2006]**

(1) ionic character (2) σ – character only (3) π –character only (4) both σ and π character

16. How many EDTA (ethylenediaminetetraacetate) molecules are required to make an octahedral complex with a Ca^{2+} ion ? **[AIEEE–2006]**

(1) One (2) Two (3) Six (4) Three

17. The "spin-only" magnetic moment [in units of Bohr magneton, (μ_B)] of Ni^{2+} in aqueous solution would be (At. No. Ni= 28)- **[AIEEE–2006]**

(1) 0 (2) 1.73 (3) 2.84 (4) 4.90

18. Which one of the following has a square planar geometry :-

(Co = 27, Ni = 28, Fe=26, Pt = 78) **[AIEEE–2007]**

(1) $[CoCl_4]^{2-}$ (2) $[FeCl_4]^{2-}$ (3) $[NiCl_4]^{2-}$ (4) $[PtCl_4]^{2-}$

19. The coordination number and the oxidation state of the element 'E' in the complex $[E(en)_2(C_2O_4^{-2})]\ NO_2^{\oplus}$ (where (en) is ethylene diamine) are, respectively - **[AIEEE–2008]**

(1) 6 and 2 (2) 4 and 2 (3) 4 and 3 (4) 6 and 3

20. In which of the following octahedral complexes of Co (at. no. 27), will the magnitude of Δ_d be the highest ? **[AIEEE–2008]**

(1) $[Co(CN)_6]^{3-}$ (2) $[Co(C_2O_4)_3]^{3-}$ (3) $[Co(H_2O)_6]^{3+}$ (4) $[Co(NH_3)_6]^{3+}$

21. Which of the following pairs represent linkage isomers ? **[AIEEE–2009]**

(1) $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$

(2) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

(3) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

(4) $[Pd\ (PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2\ (SCN)_2]$

22. Which of the following has an optical isomer? **[AIEEE–2009]**

(1) $[Co(H_2O)_4(en)]^{3+}$ (2) $[Co(en)_2(NH_3)_2]^{3+}$

(3) $[Co(NH_3)_3Cl]^{+}$ (4) $[Co(en)(NH_3)_2]^{2+}$

23. Which one of the following has an optical isomer ? **[AIEEE–2010]**

(1) $[Zn(en)_2]^{2+}$ (2) $[Zn(en)(NH_3)_2]^{2+}$ (3) $[Co(en)_3]^{3+}$ (4) $[Co(H_2O)_4(en)]^{3+}$

(en = ethylenediamine)

24. A solution containing 2.675 g of $CoCl_3.6NH_3$ (molar mass = 267.5 g mol^{-1}) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 4.78 g of AgCl (molar mass = 143.5 g mol^{-1}). The formula of the complex is :- **[AIEEE–2010]**

(At. mass of Ag = 108 u)

(1) $[CoCl(NH_3)_5]Cl_2$ (2) $[Co(NH_3)_6]Cl_3$ (3) $[CoCl_2(NH_3)_4]Cl$ (4) $[CoCl_3(NH_3)_3]$

25. Which of the following facts about the complex $[Cr(NH_3)_6]Cl_3$ is **wrong** ? **[AIEEE–2011]**

(1) The complex is an outer orbital complex

(2) The complex gives white precipitate with silver nitrate solution

(3) The complex involves d^2sp^3 hybridisation and is octahedral in shape

(4) The complex is paramagnetic

26. The magnetic moment (spin only) of $[NiCl_4]^{2-}$ is :- **[AIEEE–2011]**

(1) 2.82 BM (2) 1.41 BM (3) 1.82 BM (4) 5.46 BM

27. Among the ligands NH_3,en, CN^- and CO the **CORRECT** order of their increasing field strength, is :- **[AIEEE–2011]**

(1) $CO < NH_3 < en < CN^-$ (2) $NH_3 < en < CN^- < CO$

(3) $CN^- < NH_3 < CO < en$ (4) $en < CN^- < NH_3 < CO$

28. Which one of the following complex ions has geometrical isomers ? **[AIEEE–2011]**

(1) $[Co\ (en)_3]^{3+}$ (2) $[Ni\ (NH_3)_5Br]^{+}$

(3) $[Co\ (NH_3)_2\ (en)_2]^{3+}$(4) $[Cr\ (NH_3)_4(en)]^{3+}$

29. Which among the following will be named as dibromidobis (ethylene diamine) chromium (III) bromide ? **[AIEEE–2012]**

(1) $[Cr(en)Br_2]Br$ (2) $[Cr(en)_3]Br_3$ (3) $[Cr(en)_2Br_2]Br$ (4) $[Cr(en)Br_4]^-$

30. The complex ion
$[Pt(NO_2)\ (Py)\ (NH_3)\ (NH_2OH)]^+$ will give :- **[J-MAIN–2012, Online]**
(1) 4 isomers (Geometrical) (2) 2 isomers (Geometrical)
(3) 3 isomers (Geometrical) (4) 6 isomers (Geometrical)

31. Which of the following complex ions will exhibit optical isomerism? **[J-MAIN–2012, Online]**
(en = 1, 2-diamine ethane)
(1) $[Co(en)_2Cl_2]^+$ (2) $[Zn(en)_2]^{2+}$
(3) $[Co(NH_3)_4Cl_2]^+$ (4) $[Cr(NH_3)_2Cl_2]^+$

32. Which of the following complex species is **NOT** expected to exhibit optical isomerism ?
(1) $[Co(en)_3]^{3+}$ (2) $[Co(en)_2\ Cl_2]^+$ **[J-MAIN–2013]**
(3) $[Co(NH_3)_3\ Cl_3]$ (4) $[Co(en)\ (NH_3)_2Cl_2]^+$

33. Type of isomerism which exists between $[Pd(C_6H_5)_2(SCN)_2]$ and **[J-MAIN–2013, Online]**
$[Pd(C_6H_5)_2\ (NCS)_2]$ is :
(1) Solvate isomerism (2) Ionisation isomerism
(3) Linkage isomerism (4) Coordination isomerism

34. Which of the following is diamagnetic ? **[J-MAIN–2013, Online]**
(1) $[CoF_6]^{3-}$ (2) $[FeF_6]^{3-}$ (3) $[Fe(CN)_6]^{3-}$ (4) $[Co(Ox)_3]^{3-}$

35. The magnetic moment of the complex anion $[Cr^{I}(NO)\ (NH_3)\ (CN)_4]^{2-}$ is :**[J-MAIN–2013, Online]**
(1) 2.82 BM (2) 5.91 BM (3) 1.73 BM (4) 3.87 BM

36. The octahedral complex of a metal ion M^{3+} with four monodentate ligands L_1, L_2, L_3 and L_4 absorb wavelength in the region of red, green, yellow and blue, respectively. The increasing order of ligand strength of the four ligands is: **[J-MAIN–2014]**
(1) $L_3 < L_2 < L_4 < L_1$ (2) $L_1 < L_2 < L_4 < L_3$
(3) $L_4 < L_3 < L_2 < L_1$ (4) $L_1 < L_3 < L_2 < L_4$

37. The equation which is balanced and represents the **CORRECT** product (s) is : **[J-MAIN–2014]**
(1) $[Mg(H_2O)_6]^{2+} + (EDTA)^{4-} \xrightarrow{\text{excess NaOH}} [Mg(EDTA)]^{2+} + 6H_2O$
(2) $CuSO_4 + 4KCN \rightarrow K_2[Cu(CN)_4] + K_2SO_4$
(3) $Li_2O + 2KCl \rightarrow 2LiCl + K_2O$
(4) $[CoCl\ (NH_3)_5]^+ + 5H^+ \rightarrow Co^{2+} + 5NH_4^+ + Cl^-$

38. The **CORRECT** statement about the magnetic properties of $[Fe(CN)_6]^{3-}$ and $[FeF_6]^{3-}$ is : (Z = 26).
(1) $[Fe(CN)_6]^{3-}$ is paramagnetic, $[FeF_6]^{3-}$ is diamagnetic. **[J-MAIN–2014, Online]**
(2) both are diamagnetic.
(3) $[\ Fe(CN)_6]^{3-}$ is diamagnetic, $[FeF_6]^{3-}$ is paramagnetic.
(4) both are paramagnetic

39. An octahedral complex of Co^{3+} is diamagnetic. The hybridisation involved in the formation of the complex is : **[J-MAIN–2014]**
(1) d^2sp^3 (2) dsp^3d (3) dsp^2 (4) sp^3d^2

40. Which of the following name formula combinations is **NOT CORRECT**? **[J-MAIN–2014, Online]**

Formula	Name
(1) $K[Cr(NH_3)_2Cl_4]$	Potassium diammine Tetrachlorochromate (III)
(2) $[Co(NH_3)_4(H_2O)I]SO_4$	Tetraammine aquaiodo cobalt (III) sulphate
(3) $[Mn(CN)_5]^{2-}$	Pentacyanomagnate (II) ion
(4) $K_2[Pt(CN)_4]$	Potassium tetracyanoplatinate(II)

41. Consider the coordination compound, $[Co(NH_3)_6]Cl_3$. In the formation of this complex, the species which acts as the Lewis acid is : **[J-MAIN–2014, Online]**

(1) $[Co(NH_3)_6]^{3+}$ (2) NH_3 (3) Co^{3+} (4) $C\ell^-$

42. Among the following species the one which causes the highest CFSE, Δ_0 as a ligand is :- **[J-MAIN–2014, Online]**

(1) CN^- (2) NH_3 (3) CO (4) F^-

43. Which one of the following complexes will most likely absorb visible light ? **[J-MAIN–2014, Online]**
(At nos. Sc = 21, Ti = 22, V = 23, Zn = 30) :-

(1) $[Ti(NH_3)_6]^{4+}$ (2) $[V(NH_3)_6]^{3+}$ (3) $[Zn(NH_3)_6]^{2+}$ (4) $[Sc(H_2O)_6]^{3+}$

44. Nickel(Z = 28) combines with a uninegative monodentate ligand to form a diamagnetic complex $[NiL_4]^{2-}$. The hybridisation involved and the number of unpaired electrons present in the complex are respectively : **[J-MAIN–2014, Online]**

(1) sp^3, zero (2) sp^3. two (3) dsp^2 one (4) dsp^2, zero

45. The number of geometrical isomers that can exist for square planar $[Pt(Cl)(py)(NH_3)(NH_2OH)]^+$ is (py = pyridine) : **[J-MAIN–2015]**

(1) 4 (2) 6 (3) 2 (4) 3

46. The color of $KMnO_4$ is due to : **[J-MAIN–2015]**

(1) L $\rightarrow$ M charge transfer transition (2) $\sigma - \sigma^*$ transition
(3) M $\rightarrow$ L charge transfer transition (4) d – d transition

47. Which of the following complex ions has electrons that are symmetrically filled in both t_{2g} and e_g orbitals ? **[J-MAIN–2015, Online]**

(1) $[CoF_6]^{3-}$ (2) $[Mn(CN)_6]^{4-}$ (3) $[FeF_6]^{3-}$ (4) $[Co(NH_3)_6]^{2+}$

48. When concentrated HCl is added to an aqueous solution of $CoCl_2$, its colour changes from reddish pink to deep blue. Which complex ion gives blue colour in this reaction ?:-

(1) $[Co(H_2O)_6]^{2+}$ (2) $[CoCl_6]^{3-}$ **[J-MAIN–2015, Online]**
(3) $[CoCl_4]^{2-}$ (4) $[CoCl_6]^{4-}$

49. The **CORRECT** statement on the isomerism associated with the following complex ions,

(a) $[Ni(H_2O)_5NH_3]^{2+}$ **[J-MAIN–2015, Online]**
(b) $[Ni(H_2O)_4(NH_3)_2]^{2+}$ and
(c) $[Ni(H_2O)_3(NH_3)_3]^{2+}$ is :

(1) (a) and (b) show geometrical and optical isomerism
(2) (b) and (c) show geometrical and optical isomerism
(3) (a) and (b) show only geometrical Isomerism
(4) (b) and (c) show only geometrical Isomerism

50. Which one of the following complexes shows optical isomerism :- **[J-MAIN–2016]**

(1) $[Co(NH_3)_4Cl_2]Cl$ (2) $[Co(NH_3)_3Cl_3]$

(3) cis$[Co(en)_2Cl_2]Cl$ (4) trans$[Co(en)_2Cl_2]Cl$

(en = ethylenediamine)

51. The pair having the same magnetic moment is:- **[J-MAIN–2016]**

[At. No.: Cr = 24, Mn = 25, Fe = 26, Co = 27]

(1) $[CoCl_4]^{2-}$ and $[Fe(H_2O)_6]^{2+}$ (2) $[Cr(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$

(3) $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$ (4) $[Mn(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$

52. Which one of the following complexes will consume more equivalents of aqueous solution of $Ag(NO_3)$? **[J-MAIN–2016, Online]**

(1) $[Cr(H_2O)_6]Cl_3$ (2) $Na_2[CrCl_5(H_2O)]$ (3) $Na_3[CrCl_6]$ (4) $[Cr(H_2O)_5Cl]Cl_2$

53. Identify the **CORRECT** trend given below : **[J-MAIN–2016, Online]**

(Atomic No.= Ti : 22, Cr : 24 and Mo : 42)

(1) Δ_0 of $[Cr(H_2O)_6]^{2+} < [Mo(H_2O)_6]^{2+}$ and Δ_0 of $[Ti(H_2O)_6]^{3+} < [Ti(H_2O)_6]^{2+}$

(2) Δ_0 of $[Cr(H_2O)_6]^{2+} < [Mo(H_2O)_6]^{2+}$ and Δ_0 of $[Ti(H_2O)_6]^{3+} > [Ti(H_2O)_6]^{2+}$

(3) Δ_0 of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$ and Δ_0 of $[Ti(H_2O)_6]^{3+} > [Ti(H_2O)_6]^{2+}$

(4) Δ_0 of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$ and Δ_0 of $[Ti(H_2O)_6]^{3+} < [Ti(H_2O)_6]^{2+}$

54. $[Co_2(CO)_8]$ displays:- **[J-MAIN–2017, Online]**

(1) no Co-Co bond, four terminal CO and four bridging CO

(2) one Co-Co bond, six terminal CO and two bridging CO

(3) no Co–Co bond, six terminal CO and two bridging CO

(4) one Co-Co bond, four terminal CO and four bridging CO

55. On treatment of 100 mL of 0.1 M solution of $CoCl_3 . 6H_2O$ with excess $AgNO_3$; 1.2×10^{22} ions are precipitated. The complex is :- **[J-MAIN–2017, Offline]**

(1) $[Co(H_2O)_4 Cl_2]Cl.2H_2O$ (2) $[Co(H_2O)_3Cl_3].3H_2O$

(3) $[Co(H_2O)_6]Cl_3$ (4) $[Co(H_2O)_5Cl]Cl_2.H_2O$

56. The pair of compounds having metal in their highest oxidation state is : **[J-MAIN–2017, Online]**

(1) $[NiCl_4]^{2-}$ and $[CoCl_4]^{2-}$ (2) $[Fe(CN)_6]^{3-}$ and $[Cu(CN)_4]^{2-}$

(3) $[FeCl_4]^-$ and Co_2O_3 (4) MnO_2 and CrO_2Cl_2

57. The oxidation states of Cr in $[Cr(H_2O)_6]Cl_3$,$[Cr(C_6H_6)_2]$, and $K_2[Cr(CN)_2 (O)_2(O_2)(NH_3)]$ respectively are : **[J-MAIN–2018, Offine]**

(1) +3, +2, and +4 (2) +3, 0, and +6

(3) +3, 0, and +4 (4) +3, +4, and +6

58. Consider the following reaction and statements : **[J-MAIN–2018, Offine]**

$[Co(NH_3)_4Br_2]^+ + Br^- \rightarrow [Co(NH_3)_3Br_3] + NH_3$

(I) Two isomers are produced if the reactant complex ion is a *cis*-isomer.

(II) Two isomers are produced if the reactant complex ion is a *trans*-isomer.

(III) Only one isomer is produced if the reactant complex ion is a *trans*-isomer.

(IV) Only one isomer is produced if the reactant complex ion is a *cis*-isomer.

The correct statements are :

(1) (I) and (III) (2) (III) and (IV) (3) (II) and (IV) (4) (I) and (II)

59. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point ? **[J-MAIN–2018, Offine]**

(1) $[Co(H_2O)_5Cl]Cl_2.H_2O$

(2) $[Co(H_2O)_4Cl_2]Cl.2H_2O$

(3) $[Co(H_2O)_3Cl_3].3H_2O$

(4) $[Co(H_2O)_6]Cl_3$

60. The total number of possible isomers for square-planar $[Pt(Cl)(NO_2)(NO_3)(SCN)]^{2-}$ is :- **[J-MAIN–2018, Onine]**

(1) 16 (2) 8 (3) 24 (4) 12

61. The correct order of spin-only magnetic moments among the following is : **[J-MAIN–2018, Onine]**

(Atomic number : Mn = 25, Co = 27, Ni= 28, Zn = 30)

(1) $[ZnCl_4]^{2-} > [NiCl_4]^{2-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$

(2) $[CoCl_4]^{2-} > [MnCl_4]^{2-} > [NiCl_4]^{2-} > [ZnCl_4]^{2-}$

(3) $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [NiCl_4]^{2-} > [ZnCl_4]^{2-}$

(4) $[NiCl_4]^{2-} > [CoCl_4]^{2-} > [MnCl_4]^{2-} > [ZnCl_4]^{2-}$

62. The correct combination is **[J-MAIN–2018, Onine]**

(1) $[Ni(CN)_4]^{2-}$ – tetrahedral;

$[Ni(CO)_4]$ – paramagnetic

(2) $[NiCl_4]^{2-}$ – paramagnetic;

$[Ni(CO)_4]$ – tetrahedral

(3) $[NiCl_4]^{2-}$ – diamagnetic;

$[Ni(CO)_4]$ – square-planar

(4) $[NiCl_4]^{2-}$ – square-planar;

$[Ni(CN)_4]^{2-}$ – paramagnetic

63. Which of the following complexes will show geometrical isomerism ?**[J-MAIN–2018, Onine]**

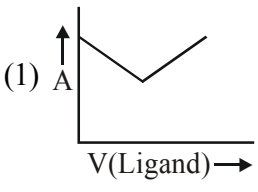
(1) Potassium amminetrichloroplatinate(II)

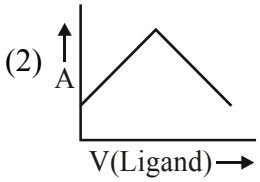
(2) Aquachlorobis (ethylenediamine) cobalt(II) chloride

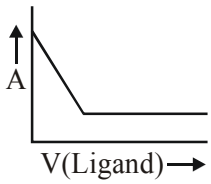
(3) Potassium tris(oxalato) chromate(III)

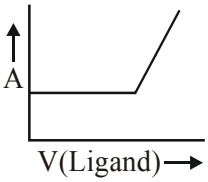
(4) Pentaaquachlorochromium(III) chloride

64. In a complexometric titration of metal ion with ligand M(Metal ion) + L(Ligand) $\rightarrow$ C(Complex) end point is estimated spectrophotometrically (through light absorption). If 'M' and 'C' do not absorb light and only 'L' absorbs, then the titration plot between absorbed light (A) versus volume of ligand 'L' (v)would look like :- **[J-MAIN–2018, Onine]**

(1) 

(2) 

(3) 

(4) 

65. In Wilkinson's catalyst, the hybridization of central metal ion and its shape are respectively

(1) dsp^2, square planar **[J-MAIN–2018, Onine]**

(2) sp^3d, trigonal bipyramidal

(3) sp^3, tetrahedral

(4) d^2sp^3, octahedral

EXERCISE # JEE-ADVANCED

1. The complex ion which has no 'd' electrons in the central metal atom is : **[JEE 2001]**
[At No. Cr = 24, Mn = 25, Fe= 26, Co = 27]
(A) $[MnO_4]^-$ (B) $[Co(NH_3)_6]^{3+}$ (C) $[Fe(CN)_6]^{3-}$ (D) $[Cr(H_2O)_6]^{3+}$

2. The **CORRECT** order of hybridisation of the central atom in the following species. **[JEE 2001]**
NH_3, $[PtCl_4]^{2-}$, PCl_5 and BCl_3 is [At No. Pt = 78]
(A) dsp^2,sp^3d,sp^2 and sp^3 (B) sp^3,dsp^2, sp^3d, sp^2
(C) dsp^2,sp^2,sp^3 and sp^3d (D) dsp^2, sp^3,sp^2 and sp^3d

3. The species having tetrahedral shape is : **[JEE 2004]**
(A) $[PdCl_4]^{2-}$ (B) $[Ni(CN)_4]^{2-}$ (C) $[Pd(CN)_4]^{2-}$ (D) $[NiCl_4]^{2-}$

4. The pair of compounds having metals in their highest oxidation state is **[JEE 2004]**
(A) MnO_2, $FeCl_3$ (B) $[MnO_4]^-$, CrO_2Cl_2
(C) $[Fe(CN)_6]^{3-}$, $[Co(CN)_3]$ (D)$[NiCl_4]^{2-}$, $[CoCl_4]^-$

5. Spin only magnetic moment of the compound Hg $[Co(SCN)_4]$ is **[JEE 2004]**
(A) $\sqrt{3}$ (B) $\sqrt{15}$ (C) $\sqrt{24}$ (D) $\sqrt{8}$

6. Which of the following pair is expected to exhibit same colour in solution? **[JEE 2005]**
(A) $VOCl_2$; $FeCl_2$ (B) $CuCl_2$; $VOCl_2$ (C) $MnCl_2$; $FeCl_2$ (D) $FeCl_2$; $CuCl_2$

7. Which type of isomerism is shown by $Co(NH_3)_4Br_2Cl$? **[JEE 2005]**
(A) Geometrical and Ionisation (B) Optical and Ionisation
(C) Geometrical and Optical (D) Geometrical only

Question No. 8 to 10 (3 questions) **[JEE 2006]**
The coordination number of Ni^{2+} is 4.
$NiCl_2$ + KCN (excess) $\rightarrow$ A (cyano complex)
$NiCl_2$ + KCl (excess) $\rightarrow$ B (chloro complex)

8. The IUPAC name of A and B are
(A) Potassium tetracyanidonickelate (II), potassium tetrachloridonickelate (II)
(B) Tetracyanidopotassiumnickelate (II), teterachloridopotassiumnickelate (II)
(C) Tetracyanidornickel (II), tetrachloridonickel (II)
(D) Potassium tetracyanidonickel (II), potassium tetrachloridonickel (II)

9. Predict the magnetic nature of A and B.
(A) Both are diamagnetic.
(B) A is diamagnetic and B is paramagnetic with one unpaired electron.
(C) A is diamagnetic and B is paramagnetic with two unpaired electrons.
(D) Both are paramagnetic.

10. The hybridization of A and B are
(A) dsp^2, sp^3 (B) sp^3, sp^3 (C) dsp^2, dsp^2 (D) sp^3d^2, d^2sp^3

11. If the bond length of CO bond in carbon monoxide is 1.128Å, then what is the value of CO bond length in $Fe(CO)_5$? **[JEE 2006]**

(A) 1.15Å (B) 1.128Å (C) 1.72Å (D) 1.118Å

12. Among the following metal carbonyls, the C–O bond order is lowest in **[JEE 2007]**

(A) $[Mn(CO)_6]^+$ (B) $[Fe(CO)_5]$ (C) $[Cr(CO)_6]$ (D) $[V(CO)_6]^-$

13. Match the complexes in Column I with their properties listed in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS.

[JEE 2007]

Column I	**Column II**
(A) $[Co(NH_3)_4(H_2O)_2]Cl_2$	(P) Geometrical isomers
(B) $[Pt(NH_3)_2Cl_2]$	(Q) Paramagnetic
(C) $[Co(H_2O)_5Cl]Cl$	(R) Diamagnetic
(D) $[Ni(H_2O)_6]Cl_2$	(S) Metal ion with 2+ oxidation state

14. Among the following, the coloured compound is **[JEE 2008]**

(A) CuCl (B) K_3 [Cu $(CN)_4$] (C) CuF_2 (D) $[Cu(CH_3CN)_4]$ BF_4

15. The IUPAC name of $[Ni(NH_3)_4]$ $[NiCl_4]$ is **[JEE 2008]**

(A) Tetrachloronickel (II)-tetraamminenickel (II)

(B) Tetraamminenickel (II)-tetrachloronickel (II)

(C) Tetraamminenickel (II)-tetrachloronickelate (II)

(D) Tetrachloronickel (II)-tetraamminenickelate (0)

16. Both $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic. The hybridisations of nickel in these complexes, respectively, are **[JEE 2008]**

(A) sp^3, sp^3 (B) sp^3, dsp^2 (C) dsp^2, sp^3 (D) dsp^2, dsp^2

17. Statement-1 : The geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ are optically inactive.

Statement-2 : Both geometrical isomers of the complex $[M(NH_3)_4Cl_2]$ possess axis of symmetry.

(A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1

(B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True **[JEE 2008]**

18. Statement-1 : $[Fe(H_2O)_5NO]SO_4$ is paramagnetic **[JEE 2008]**

Statement-2 : The Fe in $[Fe(H_2O)_5NO]SO_4$ has three unpaired electrons.

(A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1

(B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

19. The spin only magnetic moment value (in Bohr magneton units) of $Cr(CO)_6$ is **[JEE 2009]**

(A) 0 (B) 2.84 (C) 4.90 (D) 5.92

20. The compound(s) that exhibit(s) geometrical isomerism is (are) : **[JEE 2009]**

(A) $[Pt(en)Cl_2]$ (B) $[Pt(en)_2]Cl_2$ (C) $[Pt(en)_2Cl_2]Cl_2$ (D) $[Pt(NH_3)_2Cl_2]$

21. The number of water molecule(s) directly bonded to the metal centre in $CuSO_4.5H_2O$ is. **[JEE 2009]**

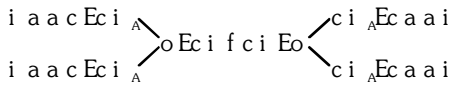
22. The ionization isomer of $[Cr(H_2O)_4Cl(NO_2)]Cl$ is – **[JEE 2010]**

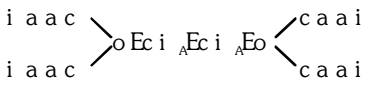
(A) $[Cr(H_2O)_4(O_2N)]Cl_2$ (B) $[Cr(H_2O)_4Cl_2](NO_2)$

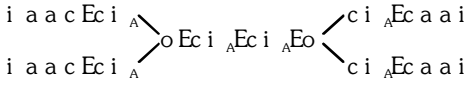
(C) $[Cr(H_2O)_4Cl(ONO)]Cl$ (D) $[Cr(H_2O)_4Cl_2(NO_2)].H_2O$

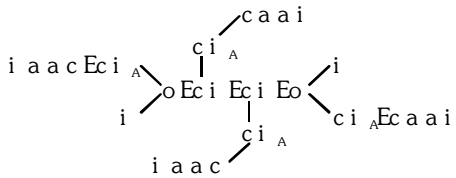
23. Total number of geometrical isomers for the complex $[RhCl(CO)(PPh_3)(NH_3)]$ is. **[JEE 2010]**

24. The correct structure of ethylenediaminetetraacetic acid (EDTA) is – **[JEE 2010]**

(A) 

(B) 

(C) 

(D) 

25. Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^-, CN^- and H_2O respectively, are - **[JEE 2011]**

(A) octahedral, tetrahedral and square planar (B) tetrahedral, square planar and octahedral

(C) square planar, tetrahedral and octahedral (D) octahedral, square planar and octahedral

26. Among the following complexes (**K–P**) **[JEE 2011]**

$K_3[Fe(CN)_6]$ (**K**), $[Co(NH_3)_6]Cl_3$ (**L**), $Na_3[Co(oxalate)_3]$ (**M**), $[Ni(H_2O)_6]Cl_2$ (**N**), $K_2[Pt(CN)_4]$ (**O**) and $[Zn(H_2O)_6](NO_3)_2$ (**P**)

The diamagnetic complex are -

(A) K, L, M, N (B) K, M, O, P (C) L, M, O, P (D) L, M, N, O

27. The volume (in mL) of 0.1M $AgNO_3$ required for complete precipitation of chloride ions present in 30 mL of 0.01M solution of $[Cr(H_2O)_5Cl]Cl_2$, as silver chloride is close to. **[JEE 2011]**

28. As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is : **[JEE 2012]**

(A) Tetraaquadiaminecobalt(III) chloride (B) Tetraaquadiamminecobalt(III) chloride

(C) Diaminetetraaquacobalt(III) chloride (D) Diammine tetraaquacobalt(III) chloride

29. The colour of light absorbed by an aqueous solution of $CuSO_4$ is - **[JEE 2012]**

(A) orange-red (B) blue-green (C) yellow (D) violet

30. $NiCl_2\{P(C_2H_5)_2(C_6H_5)\}_2$ exhibits temperature dependent magnetic behavior (paramagnetic/ diamagnetic). The coordination geometries of Ni^{2+} in the paramagnetic and diamagnetic states are respectively : **[JEE 2012]**

(A) tetrahedral and tetrahedral (B) square planar and square planar

(C) tetrahedral and square planar (D) square planar and tetrahedral

31. Consider the following complex ions P, Q and R ,
P = $[FeF_6]^{3-}$, **Q** = $[V(H_2O)_6]^{2+}$ and **R** = $[Fe(H_2O)_6]^{2+}$
The **CORRECT** order of the complex ions, according to their spin-only magnetic moment values (in B.M.) is - **[JEE 2013]**
(A) R < Q < P (B) Q < R < P (C) R < P < Q (D) Q < P < R

32. $EDTA^{4-}$ is ethylenediaminetetraacetate ion. The total number of N–Co–O bond angles in $[Co(EDTA)]^{-1}$ complex ion is **[JEE 2013]**

33. The pair(s) of coordination complex/ion exhibiting the same kind of isomerism is(are) - **[JEE 2013]**
(A) $[Cr(NH_3)_5Cl]Cl_2$ and $[Cr(NH_3)_4Cl_2]Cl$ (B) $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2(H_2O)Cl]^+$
(C) $[CoBr_2Cl_2]^{2-}$ and $[PtBr_2Cl_2]^{2-}$ (D) $[Pt(NH_3)_3(NO_3)]$ Cl and $[Pt(NH_3)_3Cl]$ Br

34. Match each coordination compound in List-I with an appropriate pair of characteristics from List-II and select the correct answer using the code given below the lists. **[JEE Adv. 2014]**
{en = $H_2NCH_2CH_2NH_2$ ' atomic numbers ; Ti = 22 ; Cr = 24 ; Co = 27 ; Pt = 78}

List-I	**List-II**
(P) $[Cr(NH_3)_4Cl_2]Cl$	(1) Paramagnetic and exhibits ionisation isomerism
(Q) $[Ti(H_2O)_5Cl](NO_3)_2$	(2) Dimagnetic and exhibits *cis-trans* isomerism
(R) $[Pt(en)(NH_3)Cl]NO_3$	(3) Paramagnetic and exhibits *cis-trans* isomerism
(S) $[Co(NH_3)_4(NO_3)_2]NO_3$	(4) Dimagnetic and exhibits ionisation isomerism

Code :

	P	**Q**	**R**	**S**		**P**	**Q**	**R**	**S**
(A)	4	2	3	1	(B)	3	1	4	2
(C)	2	1	3	4	(D)	1	3	4	2

35. A list of species having the formula XZ_4 is given below : **[JEE Adv. 2014]**
XeF_4, SF_4, SiF_4, BF_4^-, BrF_4^-, $[Cu(NH_3)_4]^{2+}$, $[FeCl_4]^{2-}$, $[CoCl_4]^{2-}$ and $[PtCl_4]^{2-}$.
Defining shape on the basis of the location of X and Z atoms, the total number of species having a square planar shape is

Subjective

36. Draw the structures of $[Co(NH_3)_6]^{3+}$, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$. Write the hybridisation of atomic orbitals of the transition metal in each case. **[JEE 2000]**

37. A metal complex having composition $Cr(NH_3)_4\ Cl_2Br$ has been isolated in two forms A and B. The form A reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia, whereas B gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of A and B and state the hybridisation of chromium in each. Calculate their magnetic moments (spin-only value). **[JEE 2001]**

38. Deduce the structures of $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ considering the hybridisation of the metal ion. Calculate the magnetic moment (spin only) of the species. **[JEE 2002]**

39. Write the IUPAC name of the compound $K_2[Cr(NO)(CN)_4(NH_3)]$. Spin magnetic moment of the complex μ = 1.73 BM. Give the structure of anion. **[JEE 2003]**

40. $NiCl_2$ in the presence of dimethyl glyoxime (DMG) gives a complex which precipitates in the presence of NH_4OH, giving a bright red colour. **[JEE 2004]**

(a) Draw its structure and show H-bonding

(b) Give oxidation state of Ni and its hybridisation

(c) Predict whether it is paramagnetic or diamagnetic

41. For the octahedral complexes of Fe^{3+} in SCN^- (thiocyanato-S) and in CN^- ligand environments, the difference between the spin only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is : [Atomic number of Fe = 26] **[JEE Ad. 2015]**

42. In the complex acetylbromidodicarbonylbis(triethylphosphine)iron(II), the number of Fe–C bond(s) is- **[JEE Ad. 2015]**

43. Among the complex ions, $[Co(NH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2)_2Cl_2]^+$, $[CrCl_2(C_2O_4)_2]^{3-}$, $[Fe(H_2O)_4(OH)_2]^+$, $[Fe(NH_3)_2(CN)_4]^-$, $[Co(NH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2)_2(NH_3)Cl]^{2+}$ and $[Co(NH_3)_4(H_2O)Cl]^{2+}$, the number of complex ion(s) that show(s) *cis-trans* isomerism is - **[JEE Ad. 2015]**

44. Among $[Ni(CO)_4]$, $[NiCl_4]^{2-}$, $[Co(NH_3)_4Cl_2]Cl$, $Na_3[CoF_6]$, Na_2O_2 and CsO_2, the total number of paramagnetic compounds is - **[JEE Ad. 2016]**

(A) 2 (B) 3 (C) 4 (D) 5

45. The number of geometric isomers possible for the complex $[CoL_2Cl_2]^-$ (L = $H_2NCH_2CH_2O^-$) is **[JEE Ad. 2016]**

46. The geometries of the ammonia complexes of Ni^{2+}, Pt^{2+} and Zn^{2+}, respectively are : **[JEE Ad. 2016]**

(A) octahedral, square planar and tetrahederal

(B) square planar, octahederal and tetrahederal

(C) tetrahederal, square planar and octahederal

(D) octahederal , tetrahederal and square planar

47. Addition of excess aqueous ammonia to a pink coloured aqueous solution of $MCl_2 . 6H_2O$ (X) and NH_4Cl gives an octahedral complex Y in the presence of air. In aqueous solution, complex Y behaves as 1 : 3 electrolyte. The reaction of X with excess HCl at room temperature results in the formation of a blue coloured complex Z. The calculated spin only magnetic moment of X and Z is 3.87 B.M., whereas it is zero for complex Y. **[JEE Ad. 2017]**

Among the following options, which statements is(are) **CORRECT** ?

(A) The hybridization of the central metal ion in Y is d^2sp^3

(B) Z is tetrahedral complex

(C) Addition of silver nitrate to Y gives only two equivalents of silver chloride

(D) When X and Z are in equilibrium at 0°C, the colour of the solution is pink

48. The correct statement(s) regarding the binary transition metal carbonyl compounds is (are) (Atomic numbers : Fe = 26, Ni = 28) **[JEE Ad. 2018]**

(A) Total number of valence shell electrons at metal centre in $Fe(CO)_5$ or $Ni(CO)_4$ is 16

(B) These are predominantly low spin in nature

(C) Metal - carbon bond strengthens when the oxidation state of the metal is lowered

(D) The carbonyl C–O bond weakens when the oxidation state of the metal is increased

49. The correct option(s) regarding the complex $[Co(en)(NH_3)_3(H_2O)]^{3+}$:- **[JEE Ad. 2018]**

(en = $H_2NCH_2CH_2NH_2$) is (are)

(A) It has two geometrical isomers

(B) It will have three geometrical isomers if bidentate 'en' is replaced by two cyanide ligands

(C) It is paramagnetic

(D) It absorbs light at longer wavelength as compared to $[Co(en)(NH_3)_4]^{3+}$

50. Match each set of hybrid orbitals from LIST-I with complex (es) given in LIST-II. **[JEE Ad. 2018]**

LIST-I	**LIST-II**
P. dsp^2	1. $[FeF_6]^{4-}$
Q. sp^3	2. $[Ti(H_2O)_3Cl_3]$
R. sp^3d^2	3. $[Cr(NH_3)_6]^{3+}$
S. d^2sp^3	4. $[FeCl_4]^{2-}$
	5. $Ni(CO)_4$
	6. $[Ni(CN)_4]^{2-}$

The correct option is

(A) P $\rightarrow$ 5; Q $\rightarrow$ 4,6; R $\rightarrow$ 2,3; S $\rightarrow$ 1

(B) P $\rightarrow$ 5,6; Q $\rightarrow$ 4; R $\rightarrow$ 3; S $\rightarrow$ 1,2

(C) P $\rightarrow$ 6; Q $\rightarrow$ 4,5; R $\rightarrow$ 1; S $\rightarrow$ 2,3

(D) P $\rightarrow$ 4,6; Q $\rightarrow$ 5,6; R $\rightarrow$ 1,2; S $\rightarrow$ 3

51. Among the species given below, the total number of diamagnetic species is____.

H atom, NO_2 monomer, O_2^- (superoxide), dimeric sulphur in vapour phase, **[JEE Ad. 2018]**

Mn_3O_4, $(NH_4)_2[FeCl_4]$, $(NH_4)_2[NiCl_4]$, K_2MnO_4, K_2CrO_4

ANSWERS KEY

EXERCISE # O-1

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A	C	B	C	C	C	D	B	D	B
Que.	11	12	13	14	15	16	17	18	19	20
Ans.	D	B	A	B	A	C	C	D	A	D
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	D	C	B	C	B	B	A	D	A	B
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	D	D	B	C	D	C	C	B	C	C
Que.	41	42	43	44	45	46	47	48	49	50
Ans.	B	C	D	D	D	D	C	B	D	B
Que.	51	52	53	54	55	56	57	58	59	60
Ans.	A	B	A	D	B	D	A	C	B	D
Que.	61	62	63	64	65	66	67	68	69	
Ans.	B	C	C	A	C	C	A	D	A	

EXERCISE # O-2

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A,B	A,B,D	A,B,C,D	A,B,D	A,B	B,C,D	A,B,C,D	A,B,C	B,C,D	A,B,C,D
Que.	11	12	13	14						
Ans.	B,D	C,D	C,D	B,D						

EXERCISE # S-1

1. (3)	**2. (2)**	**3. (9)**	**4. (36)**
5. (9)	**6. (2)**	**7. (2)**	**8. (52)**
9. (5)	**10. (2)**		

EXERCISE # S-2

Que.	1				2			
Ans.	(A)-R,	(B)-R	(C)-P	(D)-Q	(A)-P,Q,S	(B)-Q,R,S	(C)-P	(D)-P,Q
Que.	3							
Ans.	(A)-P,S	(B)-T	(C)-Q,R,T	(D)-P,S				

Que.	4	5	6	7	8	9	10	11	12	13
Ans.	B	C	D	D	C	A	C	D	D	A
Que.	14	15	16	17	18					
Ans.	D	B	B	D	D					

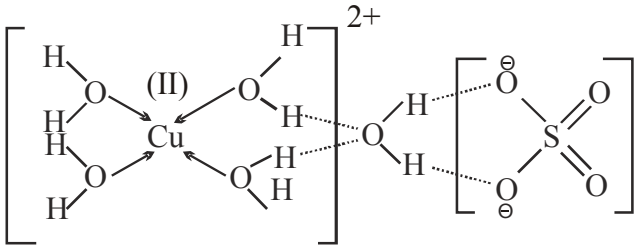
EXERCISE # J-MAIN

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	2	3	4	1	3	2	1	3	4	3
Que.	11	12	13	14	15	16	17	18	19	20
	3	1	2	4	4	1	3	4	4	1
Que.	21	22	23	24	25	26	27	28	29	30
Ans.	4	2	3	2	1	1	2	3	3	3
Que.	31	32	33	34	35	36	37	38	39	40
Ans.	1	3	3	4	3	4	4	4	1	3
Que.	41	42	43	44	45	46	47	48	49	50
Ans.	3	3	2	4	4	1	3	3	4	3
Que.	51	52	53	54	55	56	57	58	59	60
Ans.	3	1	2	2	1	2	2	1	3	4
Que.	61	62	63	64	65					
Ans.	3	2	2	4	1					

EXERCISE # J-ADVANCED

Que.	1	2	3	4	5	6	7	8	9	10
Ans.	A	B	D	B	B	B	A	A	C	A
Que.	11	12	13				14	15	16	17
Ans.	A	D	(A)-P,Q,S ; (B)-PR,S ; (C)-Q,S ; (D)-Q,S				C	C	B	B
Que.	18	19	20							
Ans.	A	A	C, D							

21.



Que.	22	23	24	25	26	27	28	29	30	31
Ans.	B	3	C	B	C	6	D	A	C	B
Que.	32	33	34	35						
Ans.	8	B, D	B	4						

36. d^2sp^3 , dsp^2 and sp^3

37. A $\rightarrow$ $[Cr(NH_3)_4ClBr]Cl$

B $\rightarrow$ $[Cr(NH_3)_4Cl_2]Br$

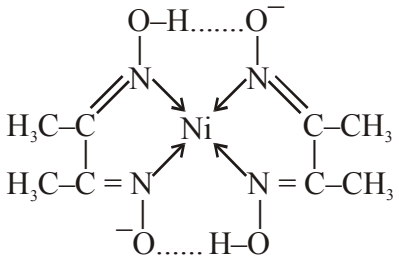
In both Cr is d^2 sp^3 hybridised and magnetic moment is $\sqrt{15}$ BM

38. $[NiCl_4]^{2-} \rightarrow sp^3$, $\sqrt{8}$ BM

$[Ni(CN)_4]^{2-} \rightarrow dsp^2$, 0

39. Potassium amminetetracyanidonitrosoniumchromate(I) $\rightarrow d^2sp^3$, octahedral

40.



dsp^2 , Ni^{2+} , diamagnetic

41. Ans. (4) **42. Ans. (3)** **43. Ans. (6)** **44. Ans. (B)**

45. Ans. (5) **46. Ans. (A)**

47. Ans. (A,B,D)

$$\underset{\text{Pink (X)}}{\overset{II}{[Co(H_2O)_6]Cl_2}} \xrightarrow[\text{Air / } O_2]{\text{Excess } NH_4OH / NH_4Cl} \underset{\text{(Y)}}{\overset{III}{[Co(NH_3)_6]Cl_3}}$$

$$\underset{\text{(X)}}{[Co(H_2O)_6]^{2+}} + \underset{\text{(excess)}}{4Cl^-} \longrightarrow \underset{\text{(Z) blue colour}}{[CoCl_4]^{2-}}$$

(A) Hybridisation of (Y) is d^2sp^3 as NH_3 is strong field ligand

(B) $[CoCl_4]^{2-}$ have sp^3 hybridisation as Cl^- is weak field ligand

(C) $\underset{\text{(Y)}}{\overset{III}{[Co(NH_3)_6]Cl_3}} + 3AgNO_3(aq.) \rightarrow 3AgCl$

(D) $\underset{\text{(Blue)}}{[CoCl_4]^{2-}} + 6H_2O \rightleftharpoons \underset{\text{(Pink)}}{[Co(H_2O)_6]^{2+}} + 4Cl^-$ $\quad \Delta H = (-)ve$ (exothermic)

When ice is added to the solution the equilibrium shifts right hence pink colour will remain predominant

So, correct answer is (A,B& D)

48. Ans.(B,C) **49. Ans.(A,B,D)** **50. Ans.(C)** **51. Ans.(1)**

METALLURGY

❑ INTRODUCTION :

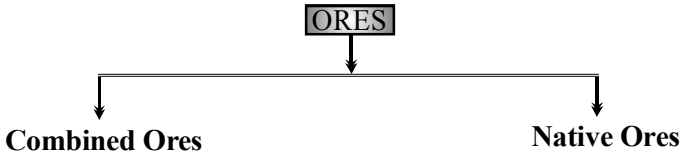
The compound of a metal found in nature is called a **mineral**.

The minerals from which metal can be economically and conveniently extracted are called **ores**.

An ore is usually contaminated with earthy or undesired materials known as **gangue**.

Note : All minerals are not ores but all ores are minerals.

Ores may be classified mainly into following two classes.



(a) ***Native ores :*** Silver, gold, platinum etc, occur as native ores.

(b) ***Combined ores :*** They contain the metal in combined form.

(i) ***Oxidised ores :*** Oxide ores , Carbonate ores, Sulphate ores, Phosphate ores, Silicate ores.

(ii) ***Sulphurised ores :*** These ores consist of sulphides of metals like iron, lead, zinc, mercury etc.

(iii) ***Halide ores :*** These ores consist of halides of metals

❑ METALLURGY :

The scientific and technological process used for the extraction/isolation of the metal from its ore is called as metallurgy.

The isolation and extraction of metals from their ores involve the following major steps:

(A) Crushing of the ore.

(B) Dressing or concentration of the ore.

(C) Isolation of the crude metal from its ore

(D) Purification or refining of the metal.

(A) Crushing and Grinding : The ore is first crushed by crushers and ground to a powder.

(B) Concentration of the ore : The removal of unwanted, useless impurities from the ore is called ***dressing, concentration or benefaction of ore.***

There are several steps for the concentration of Ores.

(I) By physical separation

(a) Gravity separation (Levigation)

(b) Froth Floatation method

(c) Magnetic separation

(i) Gravity separation or Levigation method :

It is based on the difference in the densities of the gangue and ore particles. This method is generally used for the concentration of oxide and native ores.

(ii) Electromagnetic separation :

It is based on differences in magnetic properties of the ore components.

It is used when either the ore or the impurities associated with it are magnetic in nature.

Examples :

Chromite ore($FeO.Cr_2O_3$) is separated from non–magnetic silicious impurities and cassiterite ore(SnO_2) is separated from magnetic Wolframite ($FeWO_4 + MnWO_4$).

(iii) Froth floatation process : This process is based on differential wetting of the ore by oil and gangue by water.

Examples : Galena, PbS (ore of Pb) ; copper pyrites $Cu_2S.Fe_2S_3$ or $CuFeS_2$ (ore of copper) ; zinc blende, ZnS (ore of zinc) etc.

(a) Frothers : Oil like pine oil, camphor oil etc., are used as frothers.

(b) Frothers stablizer : Aneline & Cressol

(c) Collectors : Potassium or sodium ethyl xanthate is used as a collector.

(d) Activating and depressing agents : For example galena (PbS) usually contains the minerals namely zinc blende (ZnS) and pyrites (FeS_2) as impurities. Floatation is carried out by using potassium ethyl xanthate (used as a collector) along with NaCN and Na_2CO_3 (used as depressing agent).

(II) By Chemical separation

Some of the ores are concentrated by means of chemical treatment.

Leaching : It involves the treatment of the ore with a suitable reagent. as to make it soluble while impurity remain insoluble. The ore is recovered from the solution by suitable chemical method.

(i) Bayer's process

(ii) Cyanide process

❑ CALCINATION

Calcination is a process in which ore is heated, generally in the **absence of air**, to expel water from a hydrated oxide or carbon dioxide from a carbonate at temperature below their melting points.

For Example

(i) $CaCO_3 \longrightarrow CaO + CO_2$

(ii) $Al_2O_3.\ 2H_2O \longrightarrow Al_2O_3 + 2H_2O$

❑ ROASTING

The removal of the excess sulphur contained in sulphide ores by heating **in an excess of air** is called roasting.

(Metal sulphides $\longrightarrow$ Metal oxide + SO_2)

(iii) $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + SO_2\uparrow$

❑ REDUCTION OF ORE TO THE METAL

The calcined or roasted ore is then reduced to the metallic state in either of the following ways.

(i) Reduction by Carbon (Smelting)

- Concentrate ore (ore + gangue) + R.A. (carbon) + Flux [$\therefore$ R.A. $\Rightarrow$ Reducing agent]

$\downarrow$

Metal + Slag + gases

$PbO + C \longrightarrow Pb + CO$

$Fe_2O_3 + 3C \longrightarrow Fe + 3CO$

Acidic impurity + Flux $\longrightarrow$ slag

$P_2O_5 + 3CaO \longrightarrow Ca_3(PO_4)_2$

Basic impurity + Flux $\longrightarrow$ slag

$MgCO_3 + SiO_2 \longrightarrow MgSiO_3 + CO_2\uparrow$

$FeO + SiO_2 \longrightarrow FeSiO_3$

(ii) Self Reduction

Sulphides of certain metals are reduced to metal without using any additional reducing agent. ores of Cu, Pb, Hg etc.

Self Reduction for Pb

$2PbS + 3O_2 \xrightarrow{\text{Roasting}} 2PbO + 2SO_2\uparrow$

(Galena) (air)

$PbS + 2PbO \xrightarrow[\text{Absence of air}]{\text{High temp}} 3Pb + SO_2\uparrow$

(unroasted ore) (roasted ore) (Self reduction)

(iii) Metal Displacement Method

$2Na[Au(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Au$

$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag$

Sodium tetra cyanozincate

(iv) Electrolytic Reduction

This process is mainly used for the extraction of **highly electropositive metals.**

Ex. Na, K, Mg, Ca, Al, etc.

(v) Thermite Reduction or Thermite Process

Al is used as reducing agent in this process. This process is employed in the case of those metals which have very high melting points and are to be extracted from their oxides

$Cr_2O_3 + 2Al \longrightarrow 2Cr + Al_2O_3$

$3Mn_3O_4 + 8Al \longrightarrow 9Mn + 4Al_2O_3$

❑ REFINING OF METALS

REFINING

- **(i) Thermal Refining**
  - → **(i)** Poling process (For Cu & Sn)
  - → **(ii)** Liquation method (For Sn, Pb & Bi)
  - → **(iii)** Distillation method (For Zn & Hg)
  - → **(iv)** Vapour phase refining process
    - **(a)** Van Arkel method (For Ti, Zr, Hf & B)
    - **(b)** Mond's process (For Ni)
  - → **(v)** Zone refining method (For Ge, Si, Ga & In)
  - → **(vi)** Oxidation method
    - **(a)** Bessemerization method (For Fe)
    - **(b)** Cupellation method (For Ag & Au)
  - → **(vii)** Amalgamation method (For Ag & Au)
- **(ii) Electro Refining** (Electrolysis)

EXTRACTION OF SOME INDIVIDUAL METALS

❑ EXTRACTION OF COPPER

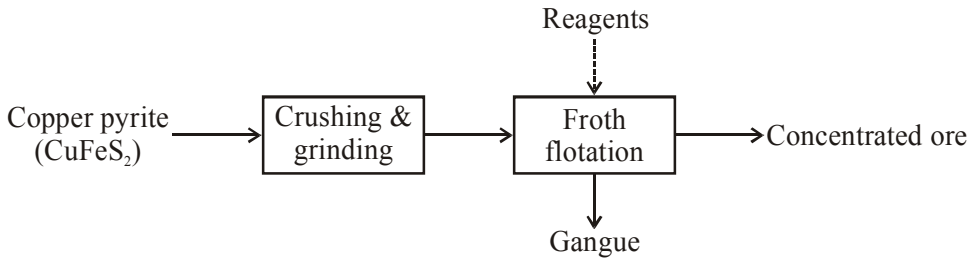
Main Ore : Copper Pyrite ($CuFeS_2$)

Extraction from pyrites by pyrometallurgical process (Smelting Process)

Some following steps are involved :

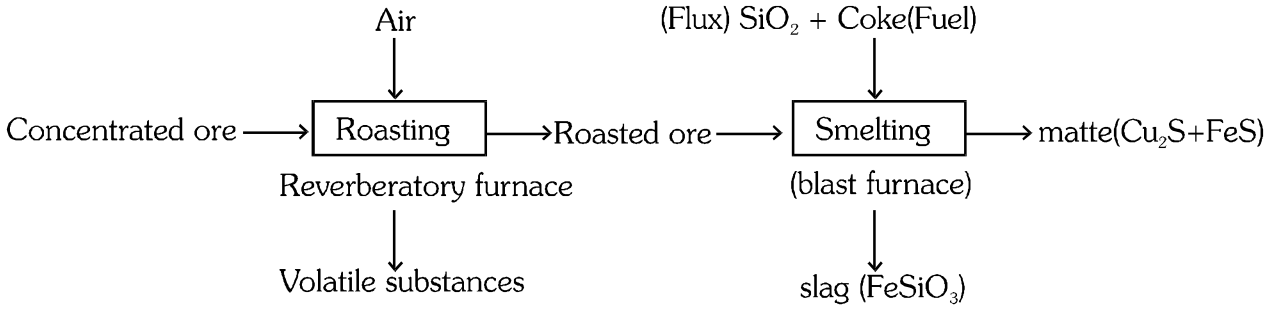
(i) Crushing & Grinding

(ii) Concentration



(iii) Roasting

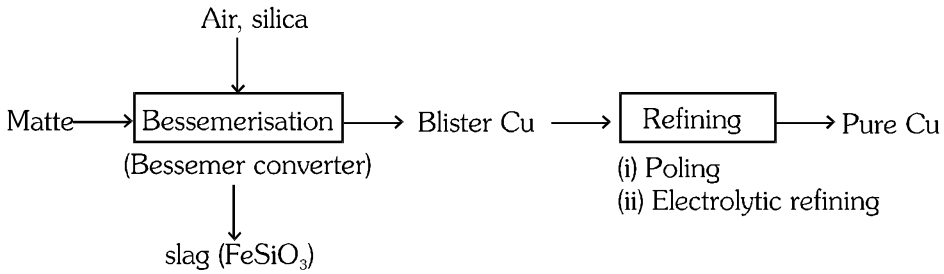
(iv) Smelting

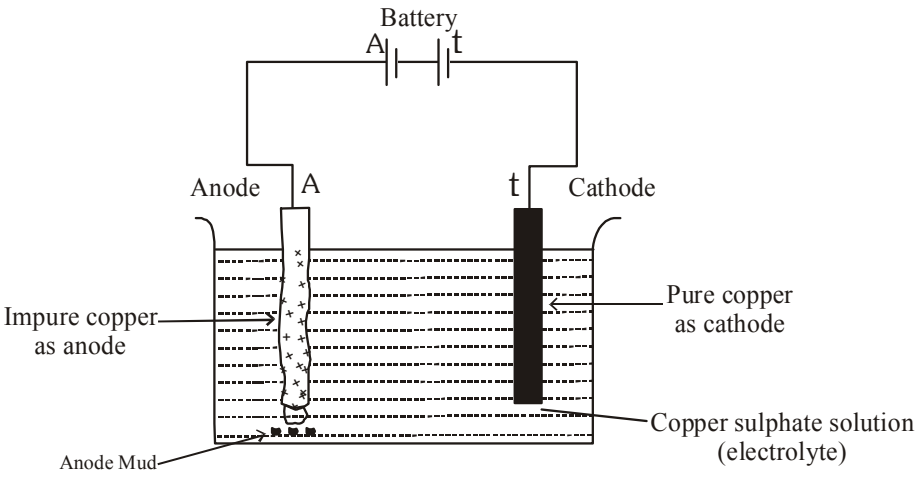


(v) Self reduction in Bessemer convertor :

(vi) Refining of copper :

(a) Poling (b) Electrolytic refining





Electrolytic refining of copper

Uses :

Copper is the second most useful metal (the first being Iron) because of its stability in air and water and excellent conductivity.

It is used :

(i) Copper is used for making wires used in electrical industry and for water and steam pipes.

(ii) For electroplating.

(iii) As a coinage alloy (with nickel) and in ornaments and jewellery.

(iv) For the manufacture of alloys like brass (Cu + Zn), bronze (Cu + Sn) German silver (Cu + Zn + Ni) bell metal (Cu + Sn) gun metal (Cu + Sn + Zn), copper coins (Cu + Zn + Sn) etc.

EXTRACTION OF LEAD

Main Ore : Galena (PbS) - There are mainly two types of process used in the extraction of Lead.

Ore - **Galena PbS** → **(a) Carbon reduction process**
→ **(b) Self reduction process**

(a) Carbon reduction process (When impurity content is high)

(i) Crushing & Grinding

(ii) Concentration by Froth floatation method

(iii) Roasting process with Lime stone ($CaCO_3$)

(iv) Smelting (Carbon reduction method with coke + Fe_2O_3)

(b) Self reduction process :- (When the impurity content is less)

(i) Crushing & Grinding

(ii) Concentration by Froth floatation method

(iii) Self reduction process

Reaction involved in self reduction :-

$PbS + O_2 \longrightarrow PbO + SO_2$

$PbS + 2PbO \longrightarrow 3Pb + SO_2$

Parallel reaction

$PbS + 2O_2 \longrightarrow PbSO_4$

$PbS + PbSO_4 \longrightarrow 2Pb + 2SO_2$

(c) Refining process :

(a) Liquation

(b) Bett's electrorefining

Anode → Impure Pb

Cathode → Pure Pb

Electrolyte → $Pb[SiF_6] + H_2SiF_6$ + Gelatin (to adjust viscosity)

on the electrolysis Pb is deposited at cathode which give 99.95% pure metal.

EXTRACTION OF ZINC

Occurrence :

Its important minerals are :

(i) Zinc blende or black jack — ZnS

(ii) Zincite — ZnO

(iii) Calamine — $ZnCO_3$

Some following steps are involved :

(i) Concentration by froth floatation method

(ii) Roasting/calcination

(iii) Smelting using carbon reduction

(iv) Electrolytic refining

Anode → Impure Zn

Cathode → Thin Al-rod

Electrolyte → Solution of $ZnSO_4 + H_2SO_4$ (dil.)

on the electrolysis zinc is deposited at cathode. The metal is scrapped off and melted to give 99.95% pure metal.

Uses :

(i) In making alloys e.g. brass, german silver, elektron (Alloy of Mg with smaller amount of Al, Y, Ag, Gd, Zn) etc.

(ii) In the extraction of silver and gold by cyanide process.

(iii) It is also used in large quantities in batteries and dry cells for making cathode container.

(iv) Zn–Cu couple, Zn- Hg, zinc dust etc. are used as reducing agent in organic reactions.

(v) large amount of zinc is used for galvanizing iron. Zinc is deposited on the surface of iron articles. This process is called galvanization.

(vi) It is also used in large quantities in batteries, as a constituent of many alloys, e.g., brass, (Cu 60%, Zn 40%) and german silver (Cu 25-30%, Zn 25-30%, Ni 40–50%).

(vii) Zinc dust is used as a reducing agent in the manufacture of dye-stuffs, paints, etc.

EXTRACTION OF TIN

Main Ore :

Cassiterite or Tinstone (SnO_2) + Major impurities [(i) SiO_2, (ii) Sulphides of Fe & Cu, (iii) $FeWO_4 + MnWO_4$]

Some following steps are involved :

(i) Crushing & Grinding :

(ii) Concentration : By gravity separation method.

(iii) Roasting : Followed by washing

(iv) Electromagnetic separation :

Thus obtained ore contains 60 – 70% SnO_2 and is called as black tin.

(vi) Carbon reduction method : Coke & Lime stone (flux) is used.

(vii) Refining method : (a) Poling (b) Electrorefining

Anode → Impure Sn

Cathode → Pure Sn

Electrolyte → ($SnSO_4$ solution + dil. H_2SO_4)

EXTRACTION OF IRON

Main Ore : *Haematite (Fe_2O_3)*

Some following steps are involved :

(i) Crushing & Grinding :

(ii) Concentration : By gravity separation method.

(iii) Roasting :

(iv) Carbon reduction (Blast furnace) : Pig iron is obtained from this process

(v) Refining : Purification of Fe can be done by different method which are as follows :

(a) Puddling Process (b) Bessemerisation Process

(c) Open hearth Process (d) L. D. Process

Thus we got pure iron.

Types of Iron

Cast iron or pig iron

It is most impure form of Iron and contains the highest proportion of carbon (2.5 - 4 %) along with traces of S, P, Mn and Si. Cast iron contain 2.5 to 4.3 & pig iron contain 2.5 to 5%.

Wrought iron (Fibrous iron) or malleable iron

It is the purest form of iron and contains minimum amount of carbon (0.12 - 0.25%) and less than 0.5% of other impurities.

Steel

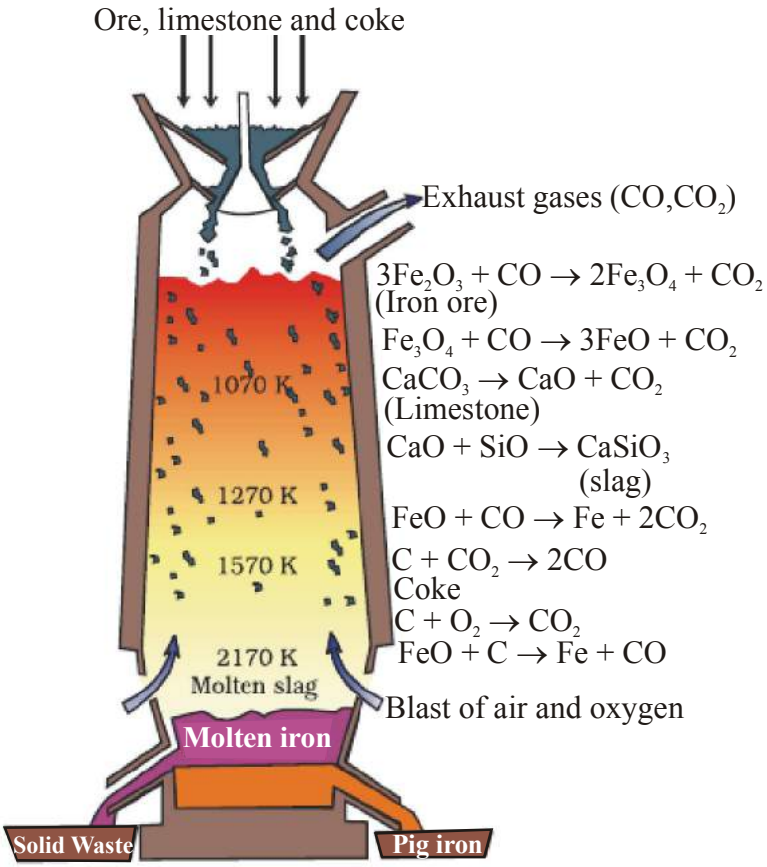
It is the most important form of iron and finds extensive applications. As far as carbon content (impurity) is concerned it is mid-way between cast iron and wrought iron, it contains 0.25- 2% carbon.

Thus all the three forms of iron differ in their carbon contents, both iron and steel are obtained from cast iron.

Order of M.P. Wrought Iron > Steel > Cast Iron or Pig Iron

% of Carbon in different type of Iron

	NAME	***% of C***
(1)	Wrought iron	0.1 to 0.25
(2)	Steel	0.25 to 2.0
(3)	Cast Iron	2.6 to 4.3
(4)	Pig Iron	2.3 to 4.6



Blast Furnace

Manufacture of Steel : The addition of different desired impurities into molten pure iron is known as steel making

Heat Treatment of Steel

(i) ***Quenching or hardening :*** Steel is heated to red hot temperature (700 to 800°C) and is then cooled suddenly by plunging into either cold water or oil. It makes steel hard and brittle.

(ii) ***Annealing :*** The steel is heated to red hot temperature (700 to 800°C) and then cooled slowly. It makes steel soft.

(iii) ***Tempering :*** If quenched steel is heated to temperature between 500 to 575 K and then cooled slowly, it becomes quite hard but brittleness disappears. The process is called tempering.

Surface treatment of steel

(i) ***Nitriding*** : Process of heating steel at 1000 K in an atmosphere of NH_3.
This gives hard coating of iron nitride on the surface.

(ii) ***Case hardening :*** Process of giving a thin coating of hardened steel, by heating steel in contact with charcoal followed quenching in oil.
– It is used for axles of railway wagons.

Uses

(i) ***Cast iron :*** It is the most important form of iron, is used for casting stoves, railway sleepers, gutter pipes , toys, etc.

(ii) It is used in the manufacture of wrought iron and steel.

(iii) ***Wrought iron :*** It is used in making anchors, wires, bolts, chains and agricultural implements.

(iv) ***Steel finds a number of uses :*** Alloy steel is obtained when other metals are added to it. Nickel steel is used for making cables, automobiles and aeroplane parts, pendulum, measuring tapes, chrome steel for cutting tools and crushing machines, and stainless steel for cycles, automobiles, utensils, pens, etc.

❑ EXTRACTION OF SILVER & GOLD

Extraction of silver :

Occurrence :

Ag found in free and combined state in nature.

Its main ore is Argentite Ag_2S.

Other ores are

Copper silver glance	–	Cu_2S . Ag_2S
Horn silver	–	AgCl
Argentiferrous lead	–	PbS(0.01 – 0.1% Ag)

Some steps are involved in the extraction of Silver metal.

(i) Crushing & Grinding :

(ii) Leaching process : Silver are extracted by the cyanide process (Mc Arthur - Forest process).

Reaction involved :

(a) $Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S \xrightarrow{+O_2+H_2O} Na_2SO_4 + 'S' + 2NaOH$

[$\because$ O_2 is used to make reaction irreversible which remove Na_2S as Na_2SO_4 + S]

(b) $2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)4] + Ag \downarrow$

(iii) Refining Process :

Anode	→	Impure Ag
Cathode	→	Pure Ag
Electrolyte	→	($AgNO_3$ solution + dil. HNO_3)

Uses :

(i) It is used in silver plating.

(ii) Silver foils are used in medicine.

(iii) Silver amalgam is used for dental filling.

(iv) Compounds of silver are used in silvering of mirrors ($AgNO_3$ + HCHO + Red Pb), in photography, as laboratory reagents etc.

(v) Silver is easily alloyed with copper, so it is used in making coins, ornaments, silver ware etc.

(vi) It gives black spot on skin due to decomposition so it is also used as hair dye and ink.

Extraction of Gold :

Occurrence : Au found in free (native) state in nature.

Same steps as are involved in the extraction of Silver metal.

(i) Crushing & Grinding :

(ii) Leaching process : Gold are extracted by the cyanide process (Mc Arthur - Forest process).

Reaction involved :

$$4Au + 8NaCN + O_2 + 2H_2O \rightleftharpoons 4Na[Au(CN)_2] + 4NaOH$$

$$2Na[Au(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Au$$

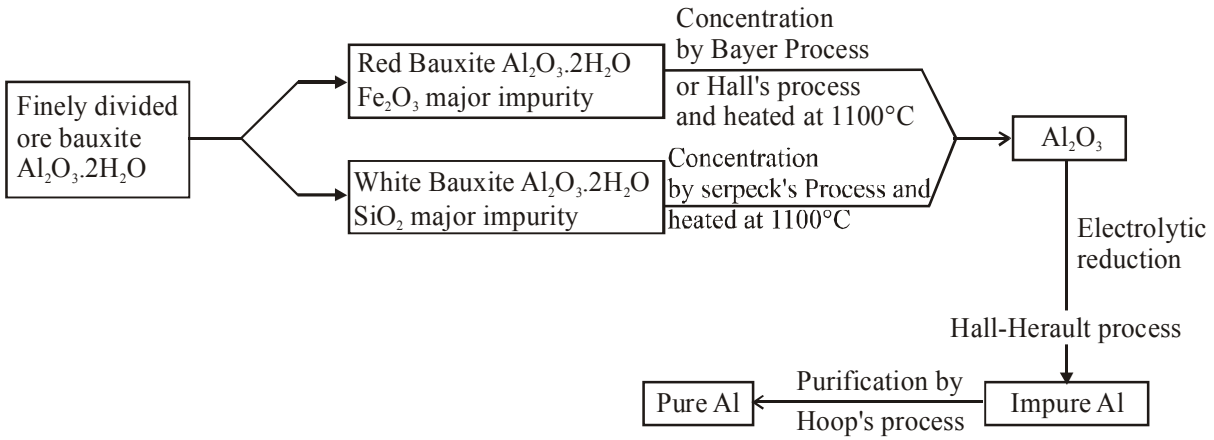
(iii) Refining Process :

Anode	→	Impure Au
Cathode	→	Pure Au
Electrolyte	→	($AuCl_3$ solution + dil. HCl)

❑ EXTRACTION OF ALUMINIUM :

Ore - Bauxite $AlO_x(OH)_{3-2x}$ (where $O < x < 1$)

Flow chart of Al from $Al_2O_3.2H_2O$ (Bauxite)



Uses

(i) Aluminium foils are used as wrappers for chocolates.

(ii) The fine dust of the metal is used in paints and lacquers.

(iii) Aluminium, being highly reactive, is also used in the extraction of chromium and manganese from their oxides.

(iv) Wires of aluminium are used as electricity conductors.

(v) Alloys containing aluminium, being light, are very useful.

❑ EXTRACTION OF MAGNESIUM :

(i) From Carnallite :

The ore is dehydrated in a current of hydrogen chloride and the mixture of fused chlorides is electrolysed.

(ii) From Magnesite :

The concentrated ore is calcined at higher temperature

$$MgCO_3 \xrightarrow[\text{Strongly}]{\text{Heated}} MgO + CO_2$$

The calcined ore is heated with coke in a current of dry chlorine gas.

$$MgO + C + Cl_2 \xrightarrow{\Delta} MgCl_2 + CO$$

The magnesium chloride is fused and then electrolysed.

$$MgO + C \text{ (Other reducing agents like Si, Al can be used)} \xrightarrow[\text{Vaccume}]{2000^\circ C} Mg + CO$$

(iii) From Sea water (Dow's process) :

Sea water contains 0.13% magnesium as chloride and sulphate. It involves following steps.

(a) *Precipitation of magnesium as magnesium hydroxide by slaked lime :*

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

(b) *Preparation of hexahydrated magnesium chloride*

$$Mg(OH)_2 + 2HCl(aq) \longrightarrow MgCl_2 + 2H_2O$$

The solution on concentration and crystallisation gives the crystals of $MgCl_2.6H_2O$

(c) *Preparation of anhydrous magnesium chloride*

$$MgCl_2.\ 6H_2O \xrightarrow[\text{Dry HCl(g)}]{\Delta\text{(calcination)}} MgCl_2 + 6H_2O$$

It is not made anhydrous by simple heating because it gets hydrolysed

$$MgCl_2.\ 6H_2O \xrightarrow{\Delta} MgO + 5H_2O + 2HCl$$

(d) *Electrolysis of fused anhydrous $MgCl_2$*

(i) Electrolyte : Molten $MgCl_2 + NaCl + CaCl_2$

(ii) Anode : Graphite electrode

(iii) Cathode : Iron cell (steel container)

Reaction occurs :

The molten mixture is electrolysed. Magnesium is liberated at the cathode (iron pot) and chlorine is evolved at graphite anode.

$MgCl_2 \rightleftharpoons Mg^{2+} + 2Cl^-$

At cathode : $Mg^{2+} + 2e^- \longrightarrow Mg(99\%\ \text{pure})$;

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

(iv) From Dolomite : In the Pidgeon Process Mg is Produced.

The concentrated ore is calcined at higher temperature

$$CaCO_3\ .\ MgCO_3 \xrightarrow{\Delta} CaO.\ MgO + 2CO_2$$

It is then reduced by ferrosilicon at 1273 K under reduced pressure.

$$2CaO.\ MgO + Fe\text{–}Si \xrightarrow{1150^\circ C} 2Mg\uparrow + Fe + Ca_2SiO_4$$

❑ THERMODYNAMICS OF REDUCTION PROCESSES (ELLINGHAM DIAGRAM)

The extraction of metals from their oxides using carbon or other metals, and by thermal decomposition, involves a number of points which merit detailed discussion.

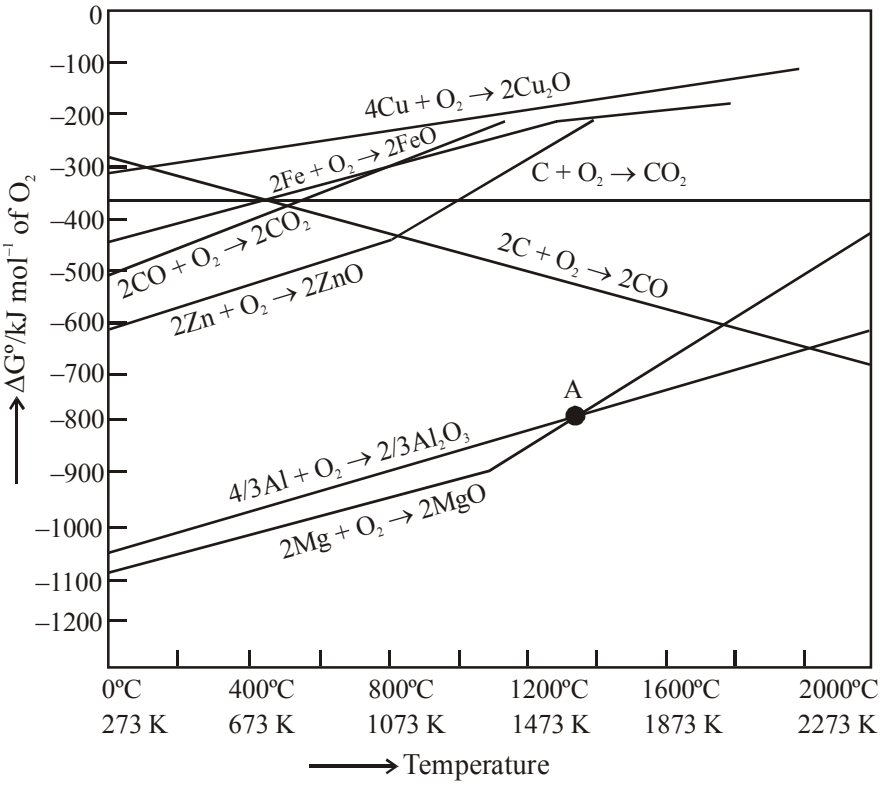
For a spontaneous reaction, the free energy change ΔG must be negative.

$$\Delta G = \Delta H - T\Delta S$$

ΔH is the enthalpy change during the reaction, T is the absolute temperature, and ΔS is the change in entropy during the reaction. Consider a reaction such as the formation of an oxide:

$$M + O_2 \rightarrow MO$$

Dioxygen is used up in the course of this reaction. Gases have a more random structure (less ordered) than liquids or solids. Consequently gases have a higher entropy than liquids or solids. In this reaction S the entropy or randomness decreases, the hence ΔS is negative. Thus if the temperature is raised then $T\Delta S$ becomes more negative. Since $T\Delta S$ is subtracted in the equation, then ΔG becomes less negative. Thus the free energy changed increases with an increase of temperature.



The free energy changes that occur when one gram molecule of a common reactant (in this case dioxygen) is used may be plotted graphically against temperature for a number of reactions of metals of their oxides. This graph is shown in figure and is called an Ellingham diagram (for oxides). Similar diagrams can be produced for one gram molecule of sulphur, giving an Ellingham diagram for sulphides, and similarly for halides.

The Ellingham diagram for oxides shows several important features:

(i) The graph for metal oxide all slope upwards, because the free energy change increases with an increase of temperature as discussed above.

(ii) The free energy changes all follows a straight line unless the materials metal or vaporize.

(iii) When the temperature is raised, a point will be reached where the graph crosses the $\Delta G = 0$ line. Below this temperature the free energy of formation of the oxide is negative, so the oxide is stable. Above this temperature the free of formation of the oxide is positive, and the oxide becomes unstable, and should decompose into the metal and dioxygen.

(iv) Any metal will reduce the oxide of other metals which lie above it in the Ellingham diagram because the free energy will become more negative by an amount equal to the different between the two graphs at that particular temperature.

Limitations of Ellingham Diagram

(i) The graph simply indicates whether a reaction is possible or not i.e., the tendency of reduction with a reducing agent is indicated. This is so because it is based only on the thermodynamic concepts. It does not say about the kinetics of the reduction process (Cannot answer questions like how fast it could be ?).

(ii) The interpretation of ΔG^{Θ} is based on K($\Delta G^{\Theta} = -RT \ln K$). Thus it is presumed that the reactants of products are in equilibrium.

Aluminium	1. Bauxite, Al_2O_3. x H_2O 2. Cryolite, Na_3AlF_6	Electrolysis of Al_2O_3 dissolved in molten Na_3AlF_6	For the extraction, a good source of electricity is required.
Iron	1. Haematite, Fe_2O_3 2. Magnetite, Fe_3O_4	Reduction of the oxide with CO and coke in Blast furnace	Temperature approaching 2170 K is required.
Copper	1. Copper pyrites, $CuFeS_2$ 2. Copper glance, Cu_2S 3. Malachite, $CuCO_3.Cu(OH)_2$ 4. Cuprite, Cu_2O	Roasting of sulphide partially and reduction	It is self reduction in a specially designed converter. The reduction takes place easily. Sulphuric acid leaching is also used in hydrometallurgy from low grade ores.
Zinc	1. Zinc blende or Sphalerite, ZnS 2. Calamine, $ZnCO_3$ 3. Zincite, ZnO	Roasting followed by reduction with coke	The metal may be purified by fractional distillation.

GENERAL PRINCIPLES & PROCESSES OF ISOLATION OF ELEMENTS

EXERCISE # O-I

ONLY ONE OPTION IS CORRECT.

ORES

1. Which of the following does not contain Mg:

(A) magnetite (B) magnesite (C) asbestos (D) carnallite

2. Which of the following is not an ore:

(A) malachite (B) calamine (C) stellite (D) cerussite

3. Carnallite does not contain

(A) K (B) Ca (C) Mg (D) Cl

4. Among the following statements, the incorrect one is

(A) calamine and siderite are carbonate ores (B) argentite and cuprite are oxide ores

(C) zinc blende and pyrites are sulphide ores (D) malachite and azurite are ores of copper

5. Select the correct statement :

(A) Magnetite is an ore of manganese (B) Pyrolusite is an ore of lead

(C) Siderite is carbonate ore of iron (D) FeS_2 is rolled gold

6. "Fool's gold" is

(A) iron pyrites (B) horn silver (C) copper pyrites (D) bronze

7. **Assertion :** Platinum and gold occur in native state in nature.

Reason : Platinum and gold are noble metals.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

CONCENTRATION METHODS

8. $Ag_2S + NaCN + Zn \longrightarrow Ag$

This method of extraction of Ag by complex formation and then its displacement is called:

(A) Parke's method (B) McArthur-Forest method

(C) Serpeck method (D) Hall's method

9. Which one of the following is not a method of concentration of ore?

(A) gravity separation (B) froth floating process

(C) electromagnetic separation (D) smelting

10. Chemical leaching is useful in the concentration of:

(A) copper pyrites (B) bauxite (C) galena (D) cassiterite

11. In froth-floatation process, pine oil functions as

(A) activator (B) frother (C) collector (D) agitator

12. Collectors are the substances which help in attachment of an ore particle to air bubble in froth. A popular collector used industrially is

(A) sodium ethyl xanthate (B) sodium xenate

(C) sodium pyrophosphate (D) sodium nitroprusside

13. In the cyanide process involving extraction of silver, zinc is used industrially as a(an)

(A) oxidising agent (B) reducing agent

(C) solvent (D) solvating agent

14. During initial treatment, preferential wetting of ore by oil and gangue by water takes place in

(A) Levigation (gravity separation) (B) Froth floatation

(C) Leaching (D) Bessemerisation

15. An non-magnetic ore containing the impurity of $FeCr_2O_4$ is concentrated by

(A) magnetic-separation (B) gravity separation

(C) froth-floatation method (D) electrostatic method

16. The beneficiation of the sulphide ores is usually done by

(A) Electrolysis (B) Smelting process

(C) Metal displacement method (D) Froth flotation method

17. The process of the isolation of a metal by dissolving the ore in aqueous solution of suitable chemical reagent followed by precipitation of the metal by a more electropositive metal is called:

(A) hydrometallurgy (B) electrometallurgy

(C) zone refining (D) electrorefining

18. Froth floatation process for concentration of ores is an illustration of the practical application of:

(A) Adsorption (B) Absorption

(C) Coagulation (D) Sedimentation

19. **Assertion :** Sulphide ores are concentrated by froth floatation process.

Reason : Pine oil acts as a frothing agent in froth floatation process.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

20. **Assertion :** Wolframite impurities are separated from cassiterite by electromagnetic separation.

Reason : Cassiterite being magnetic is attracted by the magnet and forms a separate heap.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

CALCINATION/ROASTING

21. Calcination is the process of heating the ore:

(A) in inert gas (B) in the presence of air

(C) in the absence of air (D) in the presence of CaO and MgO

22. When roasting is carried out :

(i) Sulphide ore is converted into oxide and sulphate

(ii) remove water of hydration

(iii) the ore melts (iv) arsenic and sulphur impurities are removed

Of these statements:

(A) (i), (ii) and (iii) are correct (B) (i) and (iv) are correct

(C) (i), (ii) and (iv) are correct (D) (ii), (iii) and (iv) are correct

REDUCTION PROCESS

23. In the alumino thermite process, Al acts as

(A) An oxidising agent (B) A flux

(C) A reducing agent (D) A solder

24. **Assertion :** Al is used as a reducing agent in aluminothermy.

Reason : Al has a lower melting point than Fe, Cr and Mn.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

25. Formation of metallic copper from the sulphide ore in the commercial thermo-metallurgical process essentially involves which one of the following reaction:

(A) $Cu_2S + \frac{3}{2}O_2 \longrightarrow Cu_2O + SO_2$; $CuO + C \longrightarrow Cu + CO$

(B) $Cu_2S + \frac{3}{2}O_2 \longrightarrow Cu_2O + SO_2$; $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$

(C) $Cu_2S + 2O_2 \longrightarrow CuSO_4$; $CuSO_4 + Cu_2S \longrightarrow 3Cu + 2SO_2$

(D) $Cu_2S + \frac{3}{2}O_2 \longrightarrow Cu_2O + SO_2$; $Cu_2O + CO \longrightarrow 2Cu + CO_2$

26. The element which could be extracted by electrolytic reduction of its oxide dissolved in a high temperature melt is:

(A) sodium (B) magnesium (C) fluorine (D) aluminium

27. In which of the following isolations no reducing agent is required:

(A) iron from haematite (B) Tin from cassiterite

(C) mercury from cinnabar (D) zinc from zinc blende

PURIFICATION METHODS

28. A metal has a high concentration into the earth crust and whose oxides cannot be reduced by carbon. The most suitable method for the extraction of such metal is

(A) Alumino thermite process (B) Electrolysis process

(C) Van-Arkel's process (D) Cupellation

29. **Assertion :** Alkali metals can not be prepared by the electrolysis of their chlorides in aqueous solution

Reason : Reduction potentials of alkali metals cations is much lower than that of H_2O.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

30. **Assertion :** Magnesium can be prepared by the electrolysis of aq. $MgCl_2$.

Reason : The reduction potential of Mg^{2+} is much lower than that of H_2O.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

31. Bessemerisation is carried out for

I : Fe, II : Cu, III : Al, IV : silver

(A) I , II (B) II, III (C) III, IV (D) I, III

32. In the extraction of nickel by Mond process, the metal is obtained by:

(A) electrochemical reduction (B) thermal decomposition

(C) chemical reduction by aluminium (D) reduction by carbon

33. Formation of $Ni(CO)_4$ and subsequent its decomposition into Ni and CO (recycled) makes basis of Mond's process

$$Ni + 4CO \xrightarrow{T_1} Ni(CO)_4 \xrightarrow{T_2} Ni + 4CO$$

T_1 and T_2 are:

(A) 100°C, 50°C (B) 50°C, 100°C (C) 50°C, 230°C (D) 230°C, 50°C

34. Zone refining is based on the principle of

(A) fractional distillation (B) fractional crystallisation

(C) partition coefficient (D) chromatographic separation

35. Si and Ge used for semiconductors are required to be of high purity and hence purified by

(A) zone-refining (B) electrorefining

(C) Van-Arkel's process (D) cupellation process

36. Which process of purification is represented by the following equation :

$$Ti\ (Impure) + 2I_2 \xrightarrow{250°C} TiI_4 \xrightarrow{1400°C} Ti\ (Pure) + 2I_2$$

(A) Cupellation (B) Poling (C) Van-Arkel Process (D) Zone refining

37. Which of the following employ(s) thermal decomposition of volatile iodide compounds?

(A) Thermite process (B) Hall's process (C) Van-Arkel's process (D) Mond's process

38. The method of zone refining of metals is based on the principle of:
(A) Greater mobility of the pure metal than that of impurity.
(B) Higher melting point of the impurity than that of the pure metal.
(C) Greater noble character of the solid metal than that of the impurity
(D) Greater solubility of the impurity in the molten state than in the solid

39. **Assertion :** Titanium is purified by Van-Arkel method.
Reason : Ti reacts with I_2 to form volatile TiI_4 which decomposes at 1673 K to give pure Ti.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

40. **Assertion :** Nickel is purified `by the thermal decomposition of nickel tetracarbonyl.
Reason : Nickel is a transition element.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

41. Refining of silver is done by:
(A) liquation (B) poling (C) cupellation (D) van Arkel method

42. Mercury is purified by:
(A) Passing through dilute HNO_3 (B) Distillation
(C) Distribution (D) Vapour phase refining

43. **Assertion :** Lead, tin and bismuth are purified by liquation method.
Reason : Lead, tin and bismuth have low m.p. as compared to impurities.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

44. When an impurity in a metal has greater affinity for oxygen and is more easily oxidised than the metal itself. Then, the metal is refined by
(A) cupellation (B) zone-refining (C) distillation (D) electrolytic process

EXTRACTION OF METALS

45. Which of the following process is not associated with recovery of the silver -
(A) As a side product in electrolytic refining of copper
(B) Parke's process in which Zn is used to extract silver by solvent extraction from molten lead
(C) By reaction of silver sulphide with KCN and then reaction of soluble complex with Zn
(D) By boiling $Na[Ag(CN)_2]$ aq.

46. Blister Cu is about:
(A) 60% Cu (B) 90% Cu (C) 98% Cu (D) 100% Cu

47. Iron obtained from blast furance is:
(A) wrought iron (B) cast iron (C) pig iron (D) steel

48. Which of the following term is not related to Al-extraction
(A) Serpek's process (B) Hall-Heroult process
(C) Thermite process (D) Hoop's process

49. Dow's process
(A) involves purification of copper (B) involves extraction of magnesium
(C) gives metal chloride as product (D) gives pure Na as product

50. Silica is added to roasted copper ores during extraction in order to remove
(A) cuprous sulphide (B) ferrous oxide (C) ferrous sulphide (D) cuprous oxide

51. Addition of high proportions of manganese makes steel useful in making rails of railroads, because manganese
(A) gives hardness to steel (B) helps the formation of oxides of iron
(C) can remove oxygen and sulphur (D) can show highest oxidation state of +7

52. In the commercial electrochemical process for aluminium extraction the electrolyte used is
(A) $Al(OH)_3$ in NaOH solution (B) an aqueous solution of $Al_2(SO_4)_3$
(C) a molten mixture of Al_2O_3 ,Na_3AlF_6 & CaF_2 (D) a molten mixture of Al_2O_3 and $Al(OH)_3$

53. Blister copper is refined by stirring molten impure metal with green logs of wood because such a wood liberates hydrocarbon gases (like CH_4). This process X is called _____ and the metal contains impurities of Y is _____.
(A) X = cupellation, Y = CuO_2 (B) X = poling, Y = Cu_2O
(C) X = poling, Y = CuO (D) X = cupellation, Y = CuO

54. A piece of steel is heated until redness and then plunged into cold water or oil. This treatment of steel makes it
(A) soft and malleable (B) hard but not brittle
(C) more brittle (D) hard and brittle

55. Modern method of steel manufacturing is
(A) open hearth process (B) L.D. Process
(C) Bessemerisation (D) Cupellation

56. During electrolytic reduction of alumina, two auxiliary electrolytes X and Y are added to increase the electrical conductance and lower the temperature of melt in order to making fused mixture very conducting. X and Y are
(A) cryolite and flourspar (B) cryolite and alum
(C) alum and flourspar (D) flourspar and bauxite

57. For extraction of sodium from NaCl, the electrolytic mixture NaCl + KCl + $CaCl_2$ is used. During extraction process, only sodium is deposited on cathode but K and Ca do not because
(A) Na is more reactive than K and Ca
(B) Na is less reactive than K and Ca
(C) NaCl is less stable than Na_3AlF_6 and $CaCl_2$
(D) the discharge potential of Na^+ is less than that of K^+ and Ca^{2+} ions.

58. Railway wagon axles are made by heating iron rods embedded in charcoal powder. This process is known as:
(A) Sherardising (B) Annealing (C) Tempering (D) Case hardening

59. In the extraction of copper from its sulphide ore the metal is formed by the reduction of Cu_2O with:
(A) FeS (B) CO (C) Cu_2S (D) SO_2

60. Carnallite on electrolysis gives:
(A) Ca and Cl_2 (B) Na and CO_2 (C) Al and Cl_2 (D) Mg and Cl_2

MISCELLANEOUS

61. Which of the following statement is correct regarding Cu-extraction
(A) In the smelting step carbon reduction takes places
(B) During partial roasting Cu_2S remains almost unaffected
(C) In Bessemer converter, only self reduction occur, not slag formation
(D) Blister forms in the blister Cu is due to dissolved CO_2

62. Refractory materials are generally used in furnaces because
(A) they are chemically inert (B) they can withstand high temperature
(C) they do not contain impurities (D) they decrease melting point of ore

63. Which of the following statements is correct regarding the slag formation during the extraction of a metal like copper or iron.
(A) The slag is lighter and has lower melting temperature than the metal
(B) The slag is heavier and has lower melting temperature than the metal
(C) The slag is lighter and has higher melting temperature than the metal
(D) The slag is heavier and has higher melting temperature than the metal

64. **Assertion :** Generally in smelting, roasted/cacinated ore is heated with powdered coke in presence of a flux.
Reason : Oxides are reduced to metals by C or CO. Impurities are removed as slag.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

65. **Assertion :** Magnesia and quick lime are used as basic flux.
Reason : MgO and CaO can withstand very high temperatures.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

66. **Assertion :** Wolframite impurity is separated from SnO_2 by magnetic separation
Reason : Tin stone is ferromagnetic, therefore attracted by magnet.
(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(C) Statement-1 is true, statement-2 is false.
(D) Statement-1 is false, statement-2 is true.

EXERCISE # O-2

ONE OR MORE THAN ONE OPTION MAY BE CORRECT

1. Which of the following is(are) sulphide ores?
(A) Argentite (B) Galena (C) Anglesite (D) Copper glance

2. Which of the following is(are) regarded as iron ores?
(A) Haematite (B) Magnetite (C) Limonite (D) Copper pyrites

CONCENTRATION

3. Which of the following ores is(are) concentrated by froth floatation?
(A) haematite (B) galena (C) copper pyrite (D) azurite

4. Which of the following ores is (are) concentrated industrially by froth floatation?
(A) Copper pyrites (B) Galena (C) Dolomite (D) Carnallite

5. Leaching is used for the concentration of:
(A) Red bauxite (B) Haematite (C) Gold ore (D) Silver ore

CALCINATION/ROASTING

6. Calcination and roasting processes of ores to form their oxides are beneficial
(A) to convert ores into porous form so that their reduction becomes easier
(B) as impurities like S, As, Sb, are removed
(C) as organic impurities are removed.
(D) as the ores are converted into oxide form which makes the reduction easier

7. Which of the following reaction(s) occur during calcination?
(A) $CaCO_3 \rightarrow CaO + CO_2$ (B) $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$
(C) $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$ (D) $CuS + CuSO_4 \rightarrow 2Cu + 2SO_2$

8. Which of the following is true for calcination of a metal ore?
(A) It makes the ore more porous
(B) The ore is heated to a temperature when fusion just begins
(C) Hydrated salts lose their water of crystallisation
(D) Impurities of S, As and Sb are removed in the form of their volatile oxides.

9. Roasting can be performed in
(A) blast furnace (B) reverberatory furnace
(C) electric furnace (D) None of these

REDUCTION

10. Carbon reduction method is employed for commercial extraction of metal from amongst these :
(A) haematite (B) cassiterite (C) iron pyrite (D) corundum

11. Auto reduction process is used in extraction of
(A) Cu (B) Hg (C) Al (D) Fe

12. Which of the following reduction reactions are actually employed in commerical extraction of metals?
(A) $Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$
(B) $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$
(C) $2Na[Au(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Au$
(D) $Cu_2S + Pb \rightarrow Cu + PbS \downarrow$

PURIFICATION

13. In the manufacturing of metallic sodium by fused salt-electrolysis method (Down's process), small amount of $CaCl_2$ that added is known as auxiliary electrolyte and is used to

(A) improve the electrical conductance (B) decrease the melting point of electrolyte

(C) stabilise the metallic sodium (D) increase the temperature of electrolysis

14. Poling is employed in refining of

(A) iron (B) copper (C) tin (D) lead

15. Zone refining is used for purification of

(A) Ge (B) Si (C) Ga (D) In

16. Metal(s) which does/do not form amalgam is/are

(A) Fe (B) Pt (C) Zn (D) Au

17. Metals which can be commercially extracted by smelting process

(A) Pb (B) Fe (C) Zn (D) Mg

EXTRACTION OF METALS

18. Hoop's process of purification of aluminium involves formation of layers during electrolysis. It involves

(A) the three layers have same densities but different materials.

(B) the three layers have different densities

(C) the upper layer is of pure aluminium which acts as a cathode

(D) the bottom layer is of impure aluminium which acts as an anode and middle layer consists of cryolite and BaF_2.

19. Metallurgical process of zinc involves roasting of zinc sulphide followed by reduction. Metallic zinc distills over as it is volatile and impurities like Cu, Pb and Fe gets condensed. The crude metal obtained is called spelter, which may be purified by

(A) electrolysis process (B) fractional distillation

(C) polling (D) heating with iodine

20. Which of the following process (es) are used for purification of Bauxite ore?

(A) Hall's process (B) Serpeck's process (C) Baeyer's process (D) Mond's process

21. Common impurities present in Bauxite are

(A) CuO (B) ZnO (C) Fe_2O_3 (D) SiO_2

22. Calcium silicate slag formed in extraction of iron

(A) prevents the reoxidation of molten iron.

(B) catalyses the combustion of carbon.

(C) reduces CO_2 to CO at the bottom of the furnace.

(D) is used in cement industry.

23. Amphoteric nature of aluminium is employed in which of the following process for extraction of aluminium?

(A) Baeyer's process (B) Hall's process

(C) Serpec's process (D) Dow's process

24. The chief reaction(s) occuring in blast furnace during extraction of iron from haematite is(are)

(A) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ (B) $FeO + SiO_2 \rightarrow FeSiO_3$

(C) $Fe_2O_3 + C \rightarrow 2Fe + 3CO$ (D) $CaO + SiO_2 \rightarrow CaSiO_3$

25. Which of the following are true for electrolytic extraction of aluminium

(A) cathode material contains graphite (B) anode material contains graphite

(C) cathode reacts away forming CO_2 (D) anode reacts away forming CO_2

26. During extraction of copper, it is obtained in the form of molten *matte*. Which of the following is **not true**?

(A) *matte* is further treated in Bessemer's coverter

(B) molten *matte* is electrolysed

(C) It is treated with a blast of air and sand

(D) It is dissolved in $CuSiF_6$ and crystallised.

27. The major role of fluorspar (CaF_2) which is added in small quantities in the electrolytic reduction of alumina dissolved in fused cryolite (Na_3AlF_6) is

(A) as a catalyst

(B) to make the fused mixture very conducting

(C) to lower the melting temperature of the mixture

(D) to decrease the rate of oxidation of carbon at the anode.

28. Which of the following reaction does not occur in blast furance during extraction of iron :

(A) $CaO + SiO_2 \longrightarrow CaSiO_3$ (B) $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$

(C) $FeO + SiO_2 \longrightarrow FeSiO_3$ (D) $FeO \longrightarrow Fe + \frac{1}{2}O_2$

MISCELLANEOUS

29. Which of the following employ downward movement of ore due to gravity?

(A) Gravity separation (B) Froth floatation

(C) Blast furnace (D) Bessemer's coverter

30. The **CORRECT** statements are :

(A) generally the calcination and roasting is done in blast furance

(B) the sandy and rocky materials associated with ore are called matrix

(C) froth floatation process is suitable for sulphide ores

(D) substance that reacts with gangue to form fusible mass is called slag

EXERCISE # S-1

1. Find the number of ore which are concentrated by magnetic sepration method.
Haemetite, Cassiterite, Copper Glance, Chromite, Cinnabar

2. Find the number of metals which are commercially extracted by carbon reduction method
Pb, Fe, Zn, Mg, Al, Na, Au, Ag

3. The number of following pairs is correctly matched

(i) Van Arkel method – Zirconium

(ii) Mond Process – Titanium

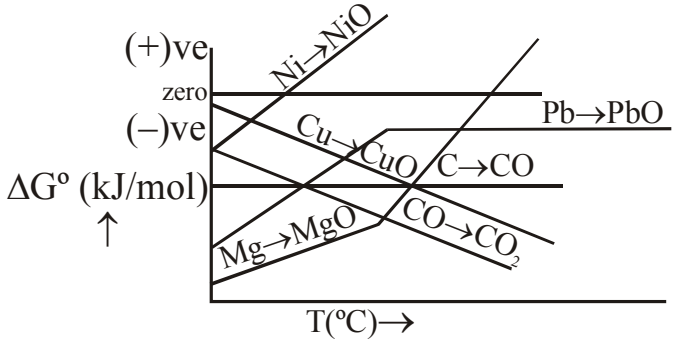
(iii) Froth Floatation Method – Cerussite

(iv) Distillation method – Zinc

(v) Poling Process – Copper

(vi) amalgamation – Gold

4. Find the number of curves which are wrongly presented in the Ellingham diagram.



5. How many of the following minerals containing Mg.
Magnetite, Carnallite, Epsom salt, Siderite

6. Find out the number of minerals given below contain iron as Fe(II).
Haematite, Magnetite, Limonite, Siderite, Chromite, Wolframite

7. Amongst the following ores, the total number of oxide ores are
Siderite, Magnetite, Haematite, Malachite, Zincite, Cuprite

8. Amongst the following, total number of sulphide ores are
Calamine, Sphalertie, Copper pyrites, Copper glance, Iron pyrites, Bauxite

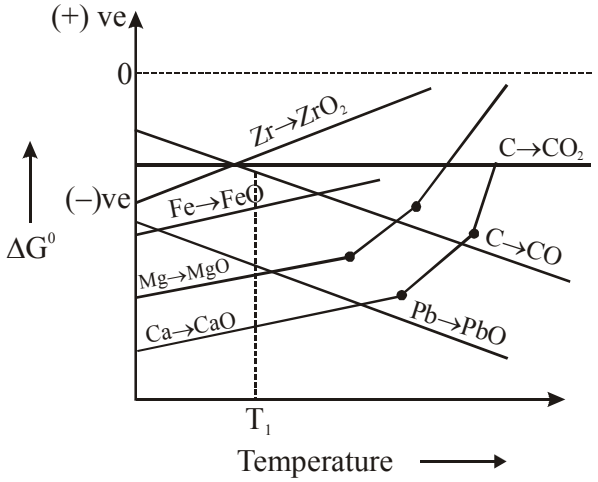
9. How many of the following ores of silver ?
Hornsilver, Cerrusite, Chalcopyrite, Galena, Anglesite, Argentite

EXERCISE # S-2

COMPREHENSION AND MATCH THE COLUMN

ELLINGHAM DIAGRAM

Paragraph for 1 to 3



1. Which of the above curve is wrongly presented -

(A) $C \rightarrow CO_2$ (B) $Pb \rightarrow PbO$ (C) $Zr \rightarrow ZrO_2$ (D) $Mg \rightarrow MgO$

2. Which of the above metal oxide is having minimum thermal decomposition temperature.

(A) CaO (B) FeO (C) ZrO_2 (D) MgO

3. Which of the following metal's oxide can be reduced by Fe as reducing agent at temperature (T_1)

(A) Zr (B) Ca (C) Mg (D) None of these

PURIFICATION METHOD

Paragraph for 4 to 5

At high temperature carbon reacts with water to produce a mixture of carbon monoxide, CO and hydrogen, H_2.

$$C + H_2O \xrightarrow{\text{red heat}} CO + H_2$$

CO is separated from H_2 and then used to separate nickel from cobalt by forming a volatile compound, nickel tetracarbony, $Ni(CO)_4$.

$$Ni + 4CO \longrightarrow Ni(CO)_4$$

4. How many moles of $Ni(CO)_4$ could be obtained from the CO produced by the reaction of 75.0g of carbon ? Assume 100% reaction and 100% recovery in both steps.

(A) 6.25 (B) 1.563 (C) 3.125 (D) 25.0

5. Formation of volatile $Ni(CO)_4$ and its subsequent heating gives pure Ni. Process is called -

(A) Hall (B) Dow (C) Serpeck (D) Mond

MISCELLANEOUS

Match Column

6. Match **Column-I** with **Column-II**

	Column-I (Metals)		**Column-II (Method used for refining)**
(A)	Iron & copper	(P)	Poling
(B)	Zirconium & Titanium	(Q)	Bessemerisation
(C)	Lead & Tin	(R)	Van-Arkel
(D)	Copper & Tin	(S)	Liquation

7. Match the following choosing one item from column X and the appropriate item from column Y.

	Column -X		**Column-Y**
(A)	Zinc from $ZnCO_3$	(P)	Calcination
(B)	Lead from PbS	(Q)	Removal of iron
(C)	Cu from $CuFeS_2$	(R)	Froth floatation process
(D)	Tin from cassiterite	(S)	Poling

8. Match column (I) (process) with column (II) (electrolyte)

	Column (I) (process)		**Column (II) (electrolyte)**
(A)	Downs cell	(P)	fused $MgCl_2$
(B)	Dow's sea water process	(Q)	fused ($Al_2O_3 + Na_3AlF_6 + CaF_2$)
(C)	Hall-Heroult	(R)	fused (40% NaCl + 60% $CaCl_2$)
		(S)	($A\ell N + C + N_2$)

9. Match column - I with column - II

	Column - I (Property)		**Column - II (Element/compound)**
(A)	Explosive	(P)	Cu
(B)	Self-reduction	(Q)	Fe_3O_4
(C)	Ferrimagnetic material	(R)	$Cu(CH_3COO)_2.Cu(OH)_2$
(D)	Verdigris	(S)	$Pb(NO_3)_2$

10. Match column - I and column - II and select the correct answer using the codes given below the lists:

	Column - I		**Column - II**
(A)	Cyanide process	(P)	Ultrapure Ge
(B)	Floatation process	(Q)	Dressing of HgS
(C)	Electrolytic reduction	(R)	Extraction of Al
(D)	Zone refining	(S)	Extraction of Au

11. Match the items of Column I with items of Column II and assign the correct code :

Column I		**Column II**	
(P)	Blistered Cu	(1)	Aluminium
(Q)	Blast furnace	(2)	$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$
(R)	Reverberatory furnace	(3)	Iron
(S)	Hall-Heroult process	(4)	$FeO + SiO_2 \rightarrow FeSiO_3$
		(5)	$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

Code : (A) P → (2) ; Q → (3) ; R → (4) ; S → (1) (B) P → (1) ; Q → (2) ; R → (3) ; S → (5)
(C) P → (5) ; Q → (4) ; R → (3) ; S → (2) (D) P → (4) ; Q → (5) ; R → (3) ; S → (2)

Answer Q.12, Q.13 and Q.14 by appropriately matching the information given in the three columns of the following table.

Column - I Extraction of metal	Column - II Methods for Reduction	Column - III Refining Method
(1) $SnO_2 \rightarrow Sn$	(i) Carbon Reduction	(P) Poling
(2) $Al_2O_3 \rightarrow Al$	(ii) Hydrometallurgic Reduction	(Q) Electrolytic Refining
(3) $Cu_2S \rightarrow Cu$	(iii) Electrolytic Reduction	(R) Distillation
(4) $ZnS \rightarrow Zn$	(iv) Self-Reduction	(S) Puddling Process

12. Which of the following is **NOT** correctly matched?

(A) (1), (iv), (S) (B) (3), (iv), (P) (C) (4), (i), (R) (D) (2), (iii), (Q)

13. Which of the followong match is the **CORRECT** reduction and purification methods for Zn

(A) (i), (R) (B) (iv), (S) (C) (iv), (P) (D) None of these

14. Which of the following set of code shows the **CORRECT** similarity with the extraction processes for Pb?

(A) (1), (ii), (S) (B) (4), (iii), (P) (C) (2), (iii), (Q) (D) (3), (iv), (Q)

EXERCISE # JEE-MAINS

1. Aluminium is extracted by the electrolysis of :- **[AIEEE-2002]**

(1) Bauxite (2) Alumina

(3) Alumina mixed with molten cryolite (4) Molten cryolite

2. Pyrolusite is a/an :- **[AIEEE-2002]**

(1) Oxide ore (2) Sulphide ore (3) Carbide ore (4) Not an ore

3. Which one of the following ores is best concentrated by froth-flotation method : **[AIEEE-2004]**

(1) Galena (2) Cassiterite (3) Magnetite (4) Malachite

4. Which of the following factors is of no significance for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly ? **[AIEEE-2008]**

(1) Metal sulphides are thermodynamically more stable than CS_2

(2) CO_2 is thermodynamically more stable than CS_2

(3) Metal sulphides are less stable than the corresponding oxides

(4) CO_2 is more volatile than CS_2

5. Which method of purification is represented by the following equation : **[AIEEE-2012]**

$$Ti(s) + 2I_2(g) \xrightarrow{523K} TiI_4(g) \xrightarrow{1700K} Ti(s) + 2I_2(g)$$

(1) Van Arkel (2) Zone refining (3) Cupellation (4) Poling

6. The substance used as froth stabilisers in froth-floatation process is : **[J-Mains-2012 (On line)]**

(1) Copper sulphate (2) Aniline

(3) Sodium cyanide (4) Potassium ethyl xanthate

7. Which of the oxide groups among the following cannot be reduced by carbon :- **[J-Mains-2012 (On line)]**

(1) Fe_3O_4, ZnO (2) PbO, Fe_3O_4 (3) Cu_2O, SnO_2 (4) CaO, K_2O

8. In Goldschmidt alumino thermic process which of the following reducing agents is used : **[J-Mains-2013 (On line)]**

(1) Calcium (2) Coke (3) Sodium (4) Al-powder

9. Calcination is the process in which :

(1) Ore is heated strongly below its melting point in the presence of excess of air and is used for the conversion of carbonates and hydrated oxide ores to their respective oxides.

(2) Ore is heated strongly below its melting point in the absence or limited supply of air and is used for conversion of sulphide ores to their respective oxides

(3) Ore is heated strongly below its melting point either in the limited supply or absence of air and is used to convert carbonates and hydrated oxide ores to their respective oxides

(4) Ore is heated strongly above its melting point in the limited supply of air to convert sulphide ores to their respective oxides.

10. The metal that cannot be obtained by electrolysis of an aqueous solution of its salts is :

[JEE-MAINS-2014]

(1) Cu (2) Cr (3) Ag (4) Ca

11. The form of iron obtained from blast furnace is : **[J-Mains-2014 (On line)]**

(1) Steel (2) Wrought Iron (3) Cast Iron (4) Pig iron

12. In the context of the Hall-Heroult process for the extraction of Al, which of the following statements is false ? **[JEE-MAINS-2015]**

(1) Al^{3+} is reduced at the cathode to form Al

(2) Na_3AlF_6 serves as the electrolyte

(3) CO and CO_2 are produced in this process

(4) Al_2O_3 is mixed with CaF_2 which lowers the melting point of the mixture and brings conductivity

13. Galvanization is applying a coating of :- **[JEE-MAINS-2016]**

(1) Zn (2) Pb (3) Cr (4) Cu

14. Which one of the following ores is best concentrated by froth floatation method ?

[JEE-MAINS-2016]

(1) Malachite (2) Magnetite (3) Siderite (4) Galena

15. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1M $ZnSO_4$? **[JEE-MAINS (Online) - 2016]**

(1) The copper metal will dissolve and zinc metal will be deposited

(2) No reaction will occur

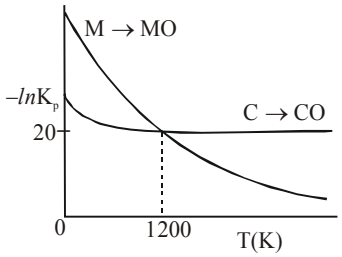
(3) The copper metal will dissolve with evolution of oxygen gas

(4) The copper metal will dissolve with evolution of hydrogen gas

16. The plot shows the variation of $-ln K_p$ versus temperature for the two reactions ?

$M(s) + \frac{1}{2}O_2(g) \rightarrow MO(s)$ and

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$



Identify the correct statement :

(1) At T > 1200 K, carbon will reduce MO(s) to M(s)

(2) At T < 1200 K, oxidation of carbon is unfavourable.

(3) Oxidation of carbon is favourable at all temperature

(4) At T < 1200 K, the reaction

$MO(s) + C(s) \rightarrow M(s) + CO(g)$ is spontaneous

17. In the leaching method, bauxite ore is digested with a concentrated solution of NaOH that produces 'X'. When CO_2 gas is passed through the aqueous solution of 'X', a hydrated compound 'Y' is precipitated. 'X' and 'Y' respectively are :- **[JEE MAIN ONLINE. 2018]**

(1) $Na[Al(OH)_4]$ and $Al_2O_3 \cdot x\ H_2O$

(2) $Al(OH)_3$ and $Al_2O_3 \cdot x\ H_2O$

(3) $Na[Al(OH)_4]$ and $Al_2(CO_3)_3 \cdot x\ H_2O$

(4) Na AlO_2 and $Al_2(CO_3)_3 \cdot x\ H_2O$

18. When metal 'M' is treated with NaOH, a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH. Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal 'M' is **[JEE MAIN OFFLINE. 2018]**

(1) Ca (2) Al (3) Fe (4) Zn

19. In the extraction of copper from its sulphide ore, metal is finally obtained by the oxidation of cuprous sulphide with :- **[JEE MAIN ONLINE. 2018]**

(1) CO (2) Cu_2O (3) Fe_2O_3 (4) SO_2

EXERCISE # JEE-ADVANCED

1. Carnallite does not contain
(A) K (B) Ca (C) Mg (D) Cl

2. During initial treatment, preferential wetting of ore by oil and gangue by water takes place in
(A) Levigation (gravity separation) (B) Froth floatation
(C) Leaching (D) Bessemerisation

3. Which of the following is true for calcination of a metal ore?
(A) It makes the ore more porous
(B) The ore is heated to a temperature when fusion just begins
(C) Hydrated salts lose their water of crystallisation
(D) Sulphur in sulphides is oxidised to SO_2
(E) Heating with carbon leads to better calcination

4. In the commercial electrochemical process for aluminium extraction, the electrolyte used as : **[JEE-1999]**
(A) $Al(OH)_3$ in NaOH solution (B) an aqueous solution of $Al_2(SO_4)_3$
(C) a molten mixture of Al_2O_3 and Na_3AlF_6 (D) a molten mixture of AlO(OH) and $Al(OH)_3$

5. The chemical process in the production of steel from haematite ore involve: **[2000 Qualifying]**
(A) reduction (B) oxidation
(C) reduction followed by oxidation (D) oxidation followed by reduction

6. Electrolytic reduction of alumina to aluminium by Hall-Heroult process is carried out:
(A) in the presence of NaCl **[2000 Qualifying]**
(B) in the presence of fluorite
(C) in the presence of cryolite which forms a melt with lower melting temperature
(D) in the presence of cryolite which forms a melt with higher melting temperature

7. The chemical composition of "slag" formed during the smelting process in the extraction of copper is : **[2001 Qualifying]**
(A) $Cu_2O + FeS$ (B) $FeSiO_3$ (C) $CuFeS_2$ (D) $Cu_2S + FeO$

8. Which of the following processes is used in extractive metallurgy of magnesium? **[2002 Qualifying]**
(A) Fused salt electrolysis (B) Self reduction
(C) Aqueous solution electrolysis (D) Thermite reduction

9. In the process of extraction of gold, **[2003 Qualifying]**

$$\text{Roasted gold ore} + CN^- + H_2O \xrightarrow{O_2} [X] + OH^-$$
$$[X] + Zn \longrightarrow [Y] + Au$$

Identify the complexes [X] and [Y] :
(A) $X = [Au(CN)_2]^-$, $Y = [Zn(CN)_4]^{2-}$ (B) $X = [Au(CN)_4]^{3-}$, $Y = [Zn(CN)_4]^{2-}$
(C) $X = [Au(CN)_2]^-$, $Y = [Zn(CN)_6]^{4-}$ (D) $X = [Au(CN)_4]^-$, $Y = [Zn(CN)_4]^{2-}$

10. The methods chiefly used for the extraction of lead and tin from their ores are respectively : **[JEE-2004]**
(A) self reduction and carbon reduction (B) self reduction and electrolytic reduction
(C) carbon reduction and self reduction (D) cyanide process and carbon reduction

11. Which ore contains both iron and copper ? **JEE-2004]**

(A) Cuprite (B) Chalcocite (C) Chalcopyrite (D) Malachite

12. Extraction for zinc from zinc blende is achieved by : **[JEE-2007]**

(A) electrolytic reduction

(B) roasting followed by reduction with carbon

(C) roasting followed by reduction with another metal

(D) roasting followed by self-reduction

13. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of :-

(A) nitrogen (B) oxygen

(C) carbon dioxide (D) argon **[JEE-2008]**

Paragraph for questions 14 to 16

Copper is the most nobel of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcanthite ($CuSO_4 . 5H_2O$), atacamite ($Cu_2Cl(OH)_3$), cuprite (Cu_2O), copper glance (Cu_2S) and malachite ($Cu_2(OH)_2CO_3$). However, 80% of the world copper production comes from the ore chalcopyrite ($CuFeS_2$). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self-reduction. **[JEE-2010]**

14. Partial roasting of chalcopyrite produces :-

(A) Cu_2S and FeO (B) Cu_2O and FeO (C) CuS and Fe_2O_3 (D) Cu_2O and Fe_2O_3

15. Iron is removed from chalcopyrite as :-

(A) FeO (B) FeS (C) Fe_2O_3 (D) $FeSiO_3$

16. In self-reduction, the reducing species is :-

(A) S (B) O^{2-} (C) S^{2-} (D) SO_2

17. Match the extraction processes listed in column I with metals listed in column II. **[JEE-2006]**

Column I	**Column II**
(A) Self reduction	(P) Lead
(B) Carbon reduction	(Q) Silver
(C) Complex formation and displacement by metal	(R) Copper
(D) Decomposition of iodide	(S) Boron

18. Match the conversions in **Column I** with the type(s) of reaction(s) given in **Column II**. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS.

Column I	**Column II** **[JEE-2008]**
(A) $PbS \rightarrow PbO$	(P) Roasting
(B) $CaCO_3 \rightarrow CaO$	(Q) Calcination
(C) $ZnS \rightarrow Zn$	(R) Carbon reduction
(D) $Cu_2S \rightarrow Cu$	(S) Self reduction

19. In extractive metallurgy of zinc partial fusion of ZnO with coke is called _____ and reduction of the ore to the molten metal is called _____ (smelting, calcining, roasting, sintering). **[JEE-1988]**

20. Extraction of metal from the ore cassiterite involves **[JEE-2011]**

(A) carbon reduction of an oxide ore (B) self-reduction of a sulphide ore

(C) removal of copper impurity (D) removal of iron impurity

21. Oxidation states of the metal in the minerals haematite and magnetite, respectively, are **[JEE-2011]**

(A) II, III in haematite and III in magnetite (B) II, III in haematite and II in magnetite

(C) II in haematite and II, III in magnetite (D) III in haematite and II, III in magnetite

22. In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agents used are : **[JEE-2012]**

(A) O_2 and CO respectively. (B) O_2 and Zn dust respectively.

(C) HNO_3 and Zn dust respectively. (D) HNO_3 and CO respectively.

23. Sulfide ores are common for the metals - **[JEE-2013]**

(A) Ag, Cu and Pb (B) Ag, Cu and Sn (C) Ag, Mg and Pb (D) Al, Cu and Pb

24. The carbon-based reduction method is **NOT** used for the extraction of **[JEE-2013]**

(A) tin from SnO_2 (B) Iron from Fe_2O_3

(C) aluminium from Al_2O_3 (D) magnesium from $MgCO_3.CaCO_3$

25. Upon heating with Cu_2S, the reagent(s) that give copper metal is/are **[JEE Adv. 2014]**

(A) $CuFeS_2$ (B) CuO (C) Cu_2O (D) $CuSO_4$

26. Copper is purified by electrolytic refining of blister copper. The correct statement(s) about this process is (are) **[JEE Adv. 2015]**

(A) Impure Cu strip is used as cathode

(B) Acidified aqueuous $CuSO_4$ is used as electrolyte

(C) Pure Cu deposits at cathode

(D) Impurities settle as anode-mud

27. Match the anionic species given in Column-I that are present in the ore(s) given in Column-II **[JEE Adv. 2015]**

Column-I	**Column-II**
(A) Carbonate	(P) Siderite
(B) Sulphide	(Q) Malachite
(C) Hydroxide	(R) Bauxite
(D) Oxide	(S) Calamine
	(T) Argentite

28. Extraction of copper from copper pyrite ($CuFeS_2$) involves **[JEE Adv. 2016]**

(A) crushing followed by concentration of the ore by froth-flotation

(B) removal of iron as slag

(C) self-reduction step to produce 'blister copper' following evolution of SO_2

(D) refining of 'blister copper' by carbon reduction

29. Galena (an ore) is partially oxidized by passing air through it at high temperature. After some time, the passage of air is stopped, but the heating is continued in a closed furnance such that the contents undergo self-reduction. The weight (in kg) of Pb produced per kg of O_2 consumed is _____ . (Atomic weights in g mol^{-1} : O = 16, S = 32, Pb = 207) **[JEE ADV. 2018]**

ANSWER KEY

EXERCISE # O-I

1. (A)	2. (C)	3. (B)	4. (B)	5. (C)	6. (A)
7. (A)	8. (B)	9. (D)	10. (B)	11. (B)	12. (A)
13. (B)	14. (B)	15. (A)	16. (D)	17. (A)	18. (A)
19. (B)	20. (C)	21. (C)	22. (C)	23. (C)	24. (B)
25. (B)	26. (D)	27. (C)	28. (B)	29. (A)	30. (D)
31. (A)	32. (B)	33. (C)	34. (B)	35. (A)	36. (C)
37. (C)	38. (D)	39. (A)	40. (B)	41. (C)	42. (B)
43. (A)	44. (A)	45. (D)	46. (C)	47. (C)	48. (C)
49. (B)	50. (B)	51. (A)	52. (C)	53. (B)	54. (D)
55. (B)	56. (A)	57. (D)	58. (D)	59. (C)	60. (D)
61. (B)	62. (B)	63. (A)	64. (A)	65. (B)	66. (C)

EXERCISE # O-II

1. (A,B,D)	2. (A,B,C)	3. (B,C)	4. (A,B)	5. (A,C,D)	6. (A,B,C,D)
7. (A, C)	8. (A, C)	9. (A, B)	10. (A, B)	11. (A,B)	12. (B, C)
13. (A,B)	14. (B,C)	15. (A,B,C, D)	16. (A,B)	17. (A,B, C)	18. (B,C,D)
19. (A,B)	20. (A,B,C)	21. (C,D)	22. (A, D)	23. (A,B)	24. (A, D)
25. (A,B,D)	26. (B,D)	27. (B,C)	28. (C,D)	29. (A,C)	30. (B, C)

EXERCISE # S-1

1. (3)	2. (3)	3. (4)	4. (4)	5. (2)	6. (4)
7. (4)	8. (4)	9. (2)			

EXERCISE # S-2

1. (B)	2. (C)	3. (A)	4. (B)	5. (D)
6. (A) Q; (B) R; (C) S; (D)P		7. (A) $\rightarrow$ P, (B) $\rightarrow$ R ; (C) $\rightarrow$ Q, R, S (D) $\rightarrow$ Q, S		
8. (A) R ; (B) P; (C) Q		9. (A) S ; (B) P; (C) Q; (D) R		
10. (A) S ; (B) Q ; (C) R ; (D) P		11. (A)	12. (A)	13. (A)	14. (D)

EXERCISE # JEE-MAINS

1. (3)	**2. (1)**	**3. (1)**	**4. (3)**	**5. (1)**	**6. (2)**
7. (4)	**8. (4)**	**9. (3)**	**10. (4)**	**11. (4)**	**12. (2)**
13. (1)	**14. (4)**	**15. (2)**	**16. (3)**	**17. (1)**	**18. (2)**
19. (2)					

EXERCISE # JEE-ADVANCED

1. (B)	**2. (B)**	**3. (A,C)**	**4. (C)**	**5. (C)**	**6. (C)**
7. (B)	**8. (A)**	**9. (A)**	**10. (A)**	**11. (C)**	**12. (B)**
13. (B)	**14. (A)**	**15. (D)**	**16. (C)**		

17. (A) – P, R ; (B) – P ; (C) – Q ; (D) – S **18. (A) – P ; (B) – Q ; (C) – P, R ; (D) – P, S**

19. Sintering , Smelting **20. (A, D) or (A, C, D)** **21. (D)**

22. (B) **23. (A)** **24. (C, D)** **25. (B, C, D)** **26. (B, C, D)**

27. (A) – P , Q , S ; (B) – T ; (C) – Q , R ; (D) – R **28. (A, B, C)**

29. Ans. (6.47)

Sol. $PbS + O_2 \longrightarrow Pb + SO_2$

$\frac{1000}{32}$ mol $\frac{1000}{32} \times 207$ gm

mol of Pb = mol of O_2

$= \frac{1000}{32}$ mol

$\therefore$ mass of Pb $= \frac{1000}{32} \times 207$g

$= \frac{207}{32}$kg $= 6.47$ kg