PREFACE

In the curricular structure introduced by this University for students of Post-Graduate degree programme, the opportunity to pursue Post-Graduate course in a subject introduced by this University is equally available to all learners. Instead of being guided by any presumption about ability level, it would perhaps stand to reason if receptivity of a learner is judged in the course of the learning process. That would be entirely in keeping with the objectives of open education which does not believe in artificial differentiation. I am happy to note that university has been recently accredited by National Assessment and Accreditation Council of India (NAAC) with grade 'A'.

Keeping this in view, study materials of the Post-Graduate level in different subjects are being prepared on the basis of a well laid-out syllabus. The course structure combines the best elements in the approved syllabi of Central and State Universities in respective subjects. It has been so designed as to be upgradable with the addition of new information as well as results of fresh thinking and analysis.

The accepted methodology of distance education has been followed in the preparation of these study materials. Co-operation in every form of experienced scholars is indispensable for a work of this kind. We, therefore, owe an enormous debt of gratitude to everyone whose tireless efforts went into the writing, editing, and devising of a proper layout of the materials. Practically speaking, their role amounts to an involvement in 'invisible teaching'. For, whoever makes use of these study materials would virtually derive the benefit of learning under their collective care without each being seen by the other.

The more a learner would seriously pursue these study materials the easier it will be for him or her to reach out to larger horizons of a subject. Care has also been taken to make the language lucid and presentation attractive so that they may be rated as quality self-learning materials. If anything remains still obscure or difficult to follow, arrangements are there to come to terms with them through the counselling sessions regularly available at the network of study centres set up by the University.

Needless to add, a great deal of these efforts are still experimental— in fact, pioneering in certain areas. Naturally, there is every possibility of some lapse or deficiency here and there. However, these do admit of rectification and further improvement in due course. On the whole, therefore, these study materials are expected to evoke wider appreciation the more they receive serious attention of all concerned.

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Inorganic Chemistry-II

Unit 1 ❑ Chemical Bonding-1

Structure

Ionic Bond

1.0 Objectives

After reading this unit you will be able to known the followings :

* Definition of ionic bonding, lattice energy.

* Details of Born-Lands equation and Born Haber Cycle.

* About Fajan's Rules and Radius Ratio Rules.

* Relation between solvation energy and solubility.

* Ionic Structure of some ionic solids.

* About stoichimetric and non stoichimetric crystal defects.

1.1 Introduction

When two atoms of same or different elements approach each other, the energy of the combination of the atoms becomes less than the sum of the energies of the two separate atoms at a large distance. We say that the two atoms have combines or a bond is formed between the two. The bond is called a chemical bond. There are different types of chemical bonds like—

* Ionic or electrovalent bond

* Covalent bond

* Co-ordinate covalent bond.

In Ionic bond formation the positively charged ions are held together by electrostatic attractions. The bond so formed is called an electrovalent or an ionic bond. The Compounds formed by the ionic bond is called ionic compounds, like NaCl, KCl, etc.

1.2 Lattice Energy

Ionic Bond: Ionic bond results from the electrostatic between two ions of opposite charge. The binding enegy of an ionic crystal, fromed by a number of ionic units, is the standrad molar entralpy change for the formation of the crystal (solid) from the constituent ions in gassom state.

$M^+_{(g)} + X^-_{(g)} \rightarrow MX_{(s)} + U$, U = Lattice energy. This standard enthilpy change for the process is actually lattice energy, that is the energy released when the constituent gaecus ions come together from infinite separation to form a solid crystal.

1.3 Born Landé Equation

The theoretical treatment of the ionic lattice energy was first introduced by Born and Landé. It follows as :

In a unit lattice of NaCl crystal (Fig. 1), the central Na^+ ion is surrounded by 6 Cl^- ions at a distance r (r = equilibrium interionic distance), 12 Na^+ ions at a distance $\sqrt{2}r$, 8 Cl^- ions at $\sqrt{3}r$ and so on.

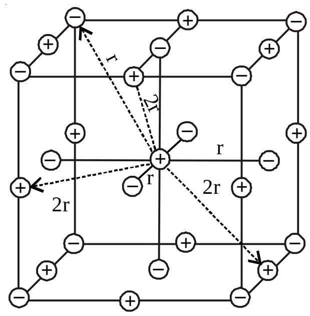


Fig. 1 Unit cell of Nacl

Thus the potential energy of the central Na^+ ion due to coalombic interaction, E_{coul} will be

$$E_{coul} \text{ (in SI units) } E_{coul} = -\frac{6e^2}{4\pi \in_0 r} + \frac{12e^2}{4\pi \in_0 \sqrt{2}r} - \frac{8e^2}{4\pi \in_0 \sqrt{3}r} + \frac{6e^2}{4\pi \in_0 2r} \cdots$$

$$= -\frac{e^2}{4\pi \in_0 r}\left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} \cdots\right] \text{...(I)J}$$

Note : $\in_0$ = epsilon

[In SI units, e(electronic charge) = 1.602×10^{-19}C,

e_0 (permitivity in vacuum) = $8.854 \times 10^{-12} C^2 N^{-1} m^{-2}$]

This series with in the bracket is a convergent one. Its limiting value is 1.74758. This is termed as Madelung constat (A), which depends on geometry of the ionic solid, but independent of ionic radius and charge. For different types of crystals, the value of A, Madelung constant are different.

'A' for different types of crystals are given below (Table 1):

Table 1 : Madelung constant values of different crystal types

Structure	A
NaCl	1.748
CsCl	1.763
Sphalerite	1.638
Wurtzite	1.641
Rutile	2.408
Flurite	2.519

The coulombic potential energy per mole of NaCl will be

$$E_{coul} = -1.748\ N_A\ e^2 / 4\pi\ \varepsilon_0 r \qquad \text{... (ii)}$$

The general expression is

$$E_{coul} = -AN_A\ e^2 / 4\pi \in_o r \qquad \text{... (iii)}$$

In addition to this coulombic interaction, there will be Pauli repulsion between the ions due to the slight overlap of their electron probability density :

E_{Rep} (per mole) = $\frac{N_A B}{r^n}$, where B is a constant and n is called Born exponent, the measure of the resistance which the ions exhibit when forced to approach each other more closely. N_A is Avogodro number. Born exponent also depends on the type of lattice. The total energy for a mole of crystal lattice of Avogadro number is :

$$U_l = E_{Coul} + E_{Rep} = -\frac{AN_A |Z^+Z^-| l_e^2}{4\pi\varepsilon_0 r} + \frac{N_A B}{r^n}$$

At equilibrium situation ($r = r_0$)

$$\frac{dU_l}{dr} = 0 = +\frac{AN_A |Z^+Z^-| e^2}{4\pi\varepsilon_0 r_0^2} - \frac{nN_A B}{r_0^{n+1}}$$

$$\text{or,}\quad \frac{AN_A\,|Z^+Z^-|\,e^2}{4\pi\varepsilon_0 r_0{}^2} = \frac{nN_A B}{r_0{}^{n+1}}$$

$$\therefore B = +\frac{AN_A\,|Z^+Z^-|\,e^2}{4\pi\varepsilon_0 n}\,r_0{}^{n-1}$$

$$\text{Now}\quad U_l = -\frac{AN_A\,|Z^+Z^-|\,e^2}{4\pi\varepsilon_0 r_0} + \frac{AN_A Z^+Z^-\,|e^2 r_0{}^{n-1}}{4\pi\varepsilon_0 r_0^n n}$$

$$\text{i.e.}\quad U_l = -\frac{AN_A\,|Z^+Z^-|\,e^2}{4\pi\varepsilon_0 r_0}\left[1-\frac{1}{n}\right] \text{...(iv)}$$

This equation is known as Born – Landé equation. The value of Born exponent, n, depends upon the principal quantum number of the electrons and hence the electronic configuration of the ions. A few representative values are given in Table 2.

Table 2 : Valus of Born exponent, n

Born enponent for different ions

Outer electronic configuration	**n**
He (IS^2)	5
Ne ($2s^2 2p^6$)	7
Ar ($3s^2 3p^6$), Cu^+ ($2s^2 3p^6 3d^{10}$)	9
Kr ($4s^2 4p^6$), Ag^+ ($4s^2 4p^6 4d^{10}$)	10
Xe ($5s^2 5p^6$), Au^+ ($5s^2 5p^6 5d^{10}$)	12

Kapustinskii Equation and its importance:

Kapustinskii proposed that for any ionic solid there exist a hypothetical rock salt structure which would be energetically equivalent to its true structure. The lattice energy of the unknown crystal may then be calculated by using 0.874 n as Madelong constant, where ‘n’ is the number of ions per formula unit. The value of $^A/_n$ increases slightly as the coordination number increases. In the case of CsCl, A/n = 1.763/2 = 0./882, C.N. = 8. Again, the radius of an ion also increaes slightly with the increase of coordination number, therefore, the ratio $^{A}/_{nr_e}$ will vary slightly for different types of crystals.

The Kapustinskii equation as given below for lattice energy of hypothetical rock salt structure (CN 6 : 6)

$$U = \frac{0.874n|Z^+Z^-|e^2N_A}{4\pi\in_0(r_+ + r_-)}\left(1 - \frac{34.5}{r_+ + r_-}\right) \text{...(2) (v)}$$

r_+ and r_- are the crystallo graphic radii of ions in pm. Putting the value of e, N_A, π and ε_0 and converging radii from pm to m, the equation (v) becomes

$$U = \frac{n|Z^+.Z^-|}{r_+ + r_-}\left(1 - \frac{34.5}{r_+ + r_-}\right) \times K \quad [K = 1.214 - 10^5 \text{ KJmol}^{-1}]$$

The Kapustinskii equation provides a simple route to calculate the lattice energy of a compound whose structure is not known only when the bonding is essentially ionic.

1.4 Born-Haber Cycle

Born-Haber-Cycle is based on Hess's law of constant heat summation which states that enthalpy of a reaction is the same whether the reaction takes place in one or several steps, which is a necessary consequence of the first law of thermodynamics concerning the conservation of energy. Born and Haber applied Hess's Law to calculate the enthalpy of formation of an ionic solid which to the algebraic summation of energy terms involved. The simple Born-Haber Cycle for the formation of NaCl crystal from the elements may be depicted as :

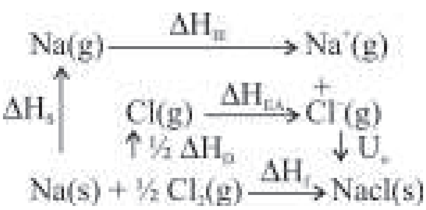


Fig. 2: Born Heber Cycle

Where,

ΔH_f = Heat of formation of the crystal.

ΔH_s = Heat of sallination enthalpy of sublimation or ethalpy of atomisation of the metal.

ΔH_D = Heat of dissociation of X_2. (here Cl_2)

ΔH_{IE} = Ionisation Energy of M (here Na)

ΔH_{EA} = Electron afficity energy of X. (here Cl

According to Hess's Law, the following is necesscity for the cycle.

$$\Delta H_f = \Delta H_s + \frac{1}{2} \Delta H_D + \Delta H_{IE} + \Delta H_{EA} + u_0$$

$$\therefore U_0 = \Delta H_f - (\Delta H_s + \frac{1}{2} \Delta H_D + \Delta H_{IE} + \Delta H_{EA}) \text{ .....(vi)}$$

The Born-Haber Cycle may be utilised to understand the stability of many ionic solids.

i) The formation of both M_g^{2+} and O^{2-} ions require very large amound of energy. Yet MgO is a stable ionic compound because its lattice energy is very high. It is a consequence of high charge on both the ions.

ii) Electron affinity of the anion may be well calculated from Born Haber Cycle when the lattice energy is previously known from Born-Landé equation.

iii) The proton affinity energy. (Proton affinity = negative of proton affinity energy i.e PA = $-\Delta H_{PA}$. For NH_3(g) e.g. PA = 886 $KJmol^{-1}$) i.e., the energy released when a proton(s) is added to a gracous species, such as

$$NH_{3(g)}{}^{+} + H_{(g)}{}^{+} = NH_4{}^{+}(g) \; \Delta H_{pA} = -886 \text{ KJ mol}^{-1}$$

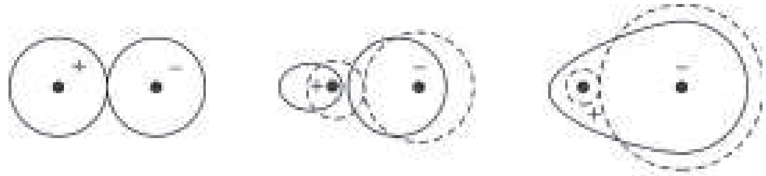
It can be shown that the proton affinity of water is greater than that of phosphine. So phosphonium compounds are readily decomposed by water./

iv) From the ionization enthalpy values of O_2 (1170 $KJmol^{-1}$) and Xe(1169 $KJmol^{-1}$), it was speculated that like $O_2{}^{+}$ species preseaf in $O_2{}^{+}$ $PtF_6{}^{-}$, Xe^{+} ion may be prepared. This lead to the idea that Xe^{+} $PtF_6{}^{-}$ might have a lattice energy sufficieat for its formation from Xe and PtF_6.

v) Stabilization of high oxidation state of retals: Metals form many fluorides with higher oxidation state than usual. Iodides combine with metal in a relatively lower oxidation state. This can be explained by the higher lattice energees of the fluorides than the iodides.

1.5 Polarising Power and Polarisability of ions

The ionic bonds and covalent bonds assumed to be totally distinct is actually an idealization. Most of the compounds are neither hundred percent ionic or hundred percent covalent. The formation of bonds intermediate in nature may occur through a process of ion deformation or polarization. When ions approach each other, the attraction of the positive field of the cation for the orbital electrons of the anion, coupled with the simultaneous repulsion of the nuclei, results in the distortion or polarisation of the anion.



(a) (b) (c)

Fig 3. Polarisation effects

(a) idealised ionpair with no polarisation (b) mutually polarised ion pair
(c) polarisation sufficient to form covalent bond.

The cation will be similarly polarised by the anion, but because of the smaller size, the effect is less pronounced. As the cations are generally smaller is size, the change density is high on the cation. Thus the polarising power of the cation is directly proportional to the charge on the cation and inversely preportional to the size of the same.

The term ionic potential (ϕ) is a measure of the polarising power of the cation:

$$\text{Ionic potential } (\phi) = \frac{\text{charge on the cation}}{\text{radius of the cation}}$$

For large value of ϕ, polarisation is greater, i.e. the bond becomes more covalent in nature. Ionic polarisation is savoured by a number of factors which are summarized in the following rules called Fajan's rules (1924):

1.5.1 Fajan's Rule

i) For small cation with high polarising power, effect of positive charge on polarising the anion will be large.

ii) Large anions have a high polarisability, since their outermost electrons are shielded from the positive nuclear field by a number of completely occupied orbitals and readily polarised by a suitable cation.

iii) For effective polarisation there should be a high charge on the cation or the anion or on both.

iv) The cation should not possess an inert gas or 18 electron configration. Inert gas electronic structure have most effective shilding of the nuclear charge.

The ionic bond will be favoured when—

a) The electronic structure of the ion is stable.

b) The charge on the ion is small.

c) A small atom forms the anion and large atom forms the cation.

The covalent bond will be favoured when—

a) The charges on the ions are high.

b) Size of the cation is small and size of the anion is large.

c) Cations have non-inert gas or pseudo inert gas configuration.

The increase in covalent character is reflected in the decreasing melting point of the compounds as illustrated in the table.

Table 3 : Variation of melting points with size and charge of the ions.

Compound	**M.P. (^{0}C)**	**Compound**	**MP(^{0}C)**	**Compound**	**MP(^{0}C)**
LiF	870	$BeCl_2$	405	AlF_3	1291
LiCl	613	$MgCl_2$	712	$AlCl_3$	180
LiBr	547	CaF_2	1392	$AlBr_3$	975
LiI	446	$CaBr_2$	730	SnF_4	705
NaF	988	CaI_2	575	$SnCl_4$	–33
NaCl	800	$CaCl_2$	772	$SnCl_2$	246
NaBr	755	$SrCl_2$	872	$PbCl_2$	501
NaI	651	$BaCl_2$	966	$PbCl_4$	–15

However other factors like packing also contributes to the melting point.

Baric Character of metal oxides also decrease with increase in ϕ, reflected in the series

$Na_2O > Li_2O > MgO > BcO$.

With increase of ϕ. Covalency in metal-oxygen fond increases and O^{2-} ion is not released in water to form OH^- ion.

1.6 Radius ratio rule

The formation of a close-packed crystal lattice of ions of different spherical size is reflected from the ratio of the radius of cation and anion.

$$\text{Radius ratio } (\rho) = \frac{r_{cation}}{r_{anion}} \left(or, \frac{r_{smaller\ ion}}{r_{larger\ ion}} \right)$$

The 'r' terms refer to radii of different ions. In a tetrahedral lattice, the size of cation exactly fitting the tetrahedral hole formed by the anions of radius r is equal to 0.225 r. Therefore a tetrahedral hole created by ions of radius r cannot accomodate any ion with radius greater than 0.225 r.

The size of the hole formed by closest packed anions may be calculated from the geometric structure, keeping in mind that in the preferred geometry, oppositely charged ions will remain in contact with each other.

For an oclahadral lattice, simple geometry allows to fix the diagonal of the square as $2r_-+2r_+$. The angle formed by the diagonal in the corner is 45°, so

$$\frac{2r^-}{2r_- + 2r_+} = \cos 45° = 0.707$$

$$r_- = 0.707\ r_- + 0.707 r_+$$

$$\text{or, } 0.293 r_- = 0.707 r_+ \quad \text{or, } \frac{r_+}{r_-} = \frac{0.293}{0.707} = 0.414$$

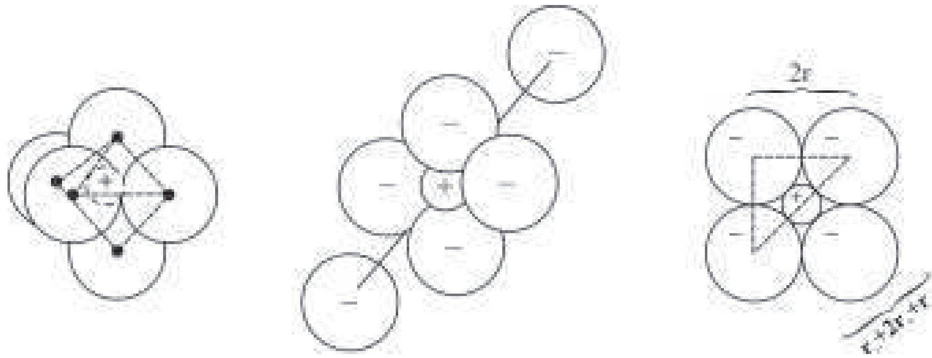


Fig. 4 Small cation in octahedral hole formed by six anions.

This is the limiting ratio, since a cation will be stable in an octahedral hole only when it is large enough to keep the anion from touching, i.e., $\frac{r_+}{r_-} \geq 0.414$ Smaller cations will preferintially fit into tetrahedral hole.

By a similar geometrical calculation, the lower limit of $\frac{r_+}{r_-}$ for a tetrahadral lattice may be determined to be $\frac{r_+}{r_-} = 0.225$. The radius ratio ranging from 0.225 to 0.414, tetrahedral structure is prefered. Above 0.414, octahedral coordination is favoured. Similarly it is possible to calculate the ratio when a cation accomodates eight anions (0.732) or twelve anions (1.000).

The use of radius ratio to govern the structure and prefered coordination number is shown below:

For beryllium sulphide, in which $\frac{r_{B^{2+}}}{r_5} = \frac{59 \text{ pm}}{170 \text{ pm}}$ =0.35. It is expected that the coordination number of Be^{2+} be 4, as the ion fits into the tetrahedral holes of the close-packed lattice. It is found experimentally that BeS adopts a wurtzite structure (Tetrehedral).

In the same way it can be predicated that sodium ions will prefer octahedral holes in a closest packed lattice of chloride ions.

$r_{N_a^+} / r_{Cl^-} = 116 \text{ pm} / 167 \text{ pm} = 0.69,$ forming NaCl structure having six coordinated sodium ions.

Applications of radius ratio rule:

(i) Prediction of crystal geometry : It is possible to predict the geometrical structure and coordination number in a particular ionic crystal of the AX by considering the limiting radius ratio. The predictions are correct when compared with experimental observations. r_+/r_- determines coordination number of cation and the coordination of anion should be same in ΔX type crystal to maintain stoichiometry.

For AX_2 type crystal as SrF_2, $\frac{r_{sr^{2+}}}{r_{F^-}} = \frac{132 \text{ pm}}{119 \text{ pm}} = 1.11$ and $\frac{r_{F^-}}{r_{Sr^{2+}}} = 0.90.$ So both can have coordination number of 8. But from stoichiometry, coordination number of Sr^{2+} must be twice that of F^-. So coordination number (C.N.) of Sr^{2+} is 8 and $F^- = 4$ in SrF_2 as in fluorite structure. In K_2O, $\frac{r_{k^+}}{r_{02-}} = \frac{152}{126} = 1.21$ and $\frac{r_{o^2}}{r_{k^+}} = 0.83$. Both can have C.N. 8, but from stoichiometry, C.N. of $O^{2-} = 8$ and C.N. of $K^+ = 4$ with antifluorite structure. For AX_2 type of crystals, the C.N. of A is predicted from limiting radius ratio rule and C.N. of X is determined by stoichiometry and C.N. of A. (See Table 4)

ii) Prediction of thermal stability of some ionic compounds : The anions will be much larger than cation for small values of r+/r– (<0.2). There will be anion-anion repulsion and bad cation-anion contact which destabilises the system. Examples of such crystan are with small cations as Li^+, Be^{2+}, Al^{3+} Mg^{2+} and large polyatomic anions as SO_4^{2-}, CO_3^{2-}, ClO_4^{2-}, NO_3^-, BF_4^-, O_2^- etc. or large monoatomic anions as Br^-, I^-. These system are thermally unstable because of inefficient crystal packing and decompose to form small anions which gives an efficient packing. For example:

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2 \ ; \ LiBF_4 \xrightarrow{\Delta} LiF + BF_3$$

$$BeSO_4 \xrightarrow{\Delta} BeO + SO_3 \ ; \ 2Na_2O_2 \xrightarrow{\Delta} Na_2O + {}^3/_2O_2$$

For a particular large anion, the thermal stability falls with decrease of r_+. So alkali metal salts of Li^+, and alkaline earth metal salts of Be^{2+} of this type are least thermally stable can also be explained by polarising power of cations).

iii) Prediction for tendency of metal ions to form hydrated salts: For salts with low r_+/r_-, there is unfavourable crystal packing (anion-anion repulsion etc.) and the cations have a tendency to get surrowded by water molecules i.e. gets hydrated, to increase the effective size of the cation. For example:

$$LiClO_4.\ 3H_2O\ (\text{or, } Li^{+}_{hyd}\ ClO_4^{-}) \text{ where } \frac{r_{+(hyd)}}{r_{-(ClO_4^-)}} >> \frac{r_{+(Li)}}{r_{-(ClO_4^-)}}$$

Alkali metal ions with larger size do not have strong tendency to from hydrated salts. (can also be explained by polasioing power of cations).

(iv) Prediction of solubility: Salts with small r_+/r_- ratio are more soluble in water. In efficient packing in crystals reduces lattice energy. Therefore solubility order of alkali metal perchlorates follow the order $LiClO_4 > NaClO_4 \gg KClO_4$, $RbClO_4$, $CsClO_4$.

v) Instability in the systems present near the limiting radius ion: The ratio r_+/r_- should be in the range 0.414 to 0.732 for octahedral coordination of cation. As the limiting value is reacted anion-anion repulsion increases and so there is a decrease in lattice energy. For NaCl type structure, LiF ($\frac{r_+}{r_-} = 0.44$) and NaI $\frac{r_+}{r_-} = 0.44$ have values close to 0.414 and are relatively unstable. This is shown by lowering of melting point and increase of solubility.

Limitations of Radius ratio rules

The radius ratio rule was worked out based on some approximations, they are:

i) The ions are considered as non-compressible hard spheres. Such approximation is not supported by quantum mechanical treatment of atoms. Many polyvalent ions as CN^-, NO_2^- etc. (except tetrahedral or actahedral moieties) are not spherical in shape.

ii) The electron clouds of adjacent ions is not affected from idealised spherical shapes lb true only for 100% ionic compounds. Actual situation is very often different from idealised situation.

iii) It is assumed that the stability of a system is not influenced by Madelung constant (which is not considered in formulating radius ratio rule. This is not true.

iv) It is assumed that crystal geometry does not affect ionic radii and the radius of an ion is an inherent property of the ion, independent of the type of crystal in which it exists. The fact is not supported by theoretical treatment (Born equation) and experimental results. It has been found that $r_4 : r_6 : r_8 = 0{\cdot}95 : 1.00 : 1.03$ where r_n is the radius of a particular ion in a geometry where C.N. around the ion is n.

v) The havier lithium halides obey the rule only marginally. For LiCl, LiBr and LiI the radius ratio lies arround 0.3, that is tetrahedral lattice is suggested. Similarly for KF, KCl, RbCl, CsF radius ratio above 0.73 corresponds to coordination number 8 or above. However, all the above salts adopt 6 : 6 coordination.

Table 4 : Radius ratio and structural type

Radius ratio	**Geometry**	**Coordination no.**	**Example**
<0.155	Linear	2	HF_2^-
0.155-0.225	Triangular	3	BO_3^{3-}, B_2O_3
0.225-0.414	Tetrahedral	4 : 4	ZnS
0.414-0.732	Octahedral	6.6	NaCl, NiAs
		6 : 3	TiO_2
		8.8	CsCl
0.732-1.0	Cubic	8 : 4	CaF_2, UO_2

Example: Calculate the minimum value of r_+/r_- required for coordination number four:

$OA = OB = OC = r_+ + r_-$, $AB = BC = 2r_-$

BOM is a right angled triangle where BM = MC = r, OM bisects the angle ∠BOC = 109.5°, ∠BOM = 54.75. In the Triangle BOM, Sin 54.75 = BM/BO = r+/r_++r_-. This gives r_+/r_- = 0.225.

1.7 Solvation Energy and Solubility Energetics of dissolution process

To dissolve an electrolyte in a suitable solvent, the primary requirement is to overcome the lattice energy of the ionic crystal. The energy is compensated from the solvation energy of the ions. In the solutioue, the ions get solvated and the energy evolved during solvation must be greater than the lattice energy of the crystal.

$$MX \xrightarrow{\text{Solvent}} M^+_{sol} + X^-_{sol} + \text{energy } (E_{sol})$$

The solvation process occurs by the electrostate interaction between the solute ion and the solvent molecules (ion-dipole interaction). When the solvent is polar, the negative end of the solvent molecule is coordinated to the cation. In case of water like solvents, the ions are separated by the solvent molecules of high dielectric constant $(\in)$ $\left(e_{H_2O} = 81.7 \in_0\right)$.

The process of dissolution of an ionic compound in water may be depicted by a born Haber cycle:

Two factors will contribute to the maguitude of solvation: (i) inherent ability of the solvent to coordinate strongly to the ions involved. (ii) type of ions involved, particularly the size. The forces in the lattice are stranger (ion-ion) than those holding the solvent molecale to the ion (ion-dipole). But there are several of the latter interaction for each ion. As a result, the enthalpy of solvation is roughly of the same order of magnitude as the lattice energy. Therefore the total enthalpy of the solution can be either +ve or –ve, depending upon the specific salt. When the enthalpy of the solution is –ve and the entropy of solution is +ve, the free energy of solution is favourable as the enthalpy and entropy of solution reinforce each other.

When enthalpy of solution for ionic compound is +ve, the temperature drops on dissolution in water.

If the enthalpy is sufficiently positive, favourable entropy may not be able to overcome it and the compound will be insolable in water, e.g., $KClO_4$.

From Born-Landé equation, Lattice energy is inversely proportional to the sum of radii of the ions.

$$U = f.\left(\frac{1}{r_+ + r_-}\right)$$

But enthalpy of hydration depends on individual ion,

$$\Delta H_{thyd} = f_2\left(\frac{1}{r_+}\right) + f_3\left(\frac{1}{r_-}\right)$$

It is clean that two functions will respond differently to the variation in r_+ and r_-.

Lattice Energy is favoured when ions are smaller is size. In contrast, the hydration enthalpy is the sum of the enthalpies of two individual ions. If one of them is very large ($r_- \gg r_+$ or $r_+ \gg r_-$) the total may be stabilized. Therefore lattice energy will be favoured more when r+yr_ compared to ΔH_{hyd}. So ionic compounds with comparable sizes of cation and anion have high lattice energy compared to hydration energy and so their solubility is disfavoured. In contrast, ionic solids with dissimilar sized ions have comparatively lower lattice energy and are favourable for dissolution. Though the larger ion may have lower hydration energy, the smaller counter ion have higher hydration energy which overcomes the lattice energy to favour dissolution. This fact is related to crystal packing efficiency. For dissimilar sized ions in the lattice, packing is inefficient and there is a repulsion among the larger sized ions of same charge to distabilise the crystal. The effect may be seen from the solubility of alkali halides in solution: LiF is the least soluble of the Lithium halides, as well as the least soluble alkali fluoride. CsI is the least soluble cesium halide and the least soluble alkali iodide, LiF and CsI haved comparable sized ions, so least soluble. CsF is the highest soluble alkali halide.

There is a very practical consequence of the relation of solubility to size. It is often possible to prepare a large complex ion with a metal and several ligands which is stable in solution but it is difficult to isolate the large comple ion. Only when a large counter ion is introduced, the precipitation is possible.

In qualilative idea:

$$\Delta H_{solution} = \Delta H_{solute\text{-}solvent} - \Delta H_{Solute\text{-}solute} - \Delta H_{solvent\text{-}solvent}$$

Where the various energies result from ion-ion, ion-dipole, ion-induced dipole, dipole-dipole and London forces. $\Delta H_{solution} < O$ and $O > T\Delta S_{solu}$ favours solubility.

1.8 Packing in crystals, packing efficiency

The structural type of a crystal is well understood from the unit lattice which on infinite repitition produces the total structure of the crystal. A closed packed structure in attained with minimum unfilled space. Ionic crystals are close-packed assembly of oppositely charged ions of different sizes.

The simplest type of structure is cubic lattice. Substituting the lattice points, for simplicity, by eight equal sized spheres gives the arrangement shown in the figure 5(a). In the extended lattice, each corner-sphere will be shared by eight cubes, four in the same layer and four above. So total contribution of the lattice points per unit cell is $8\times\frac{1}{8}=1$. Hence the effective volume occupied within the cube is equal to the volume of $8\times\frac{1}{8}$ or one sphere. If the radius of each sphere is r, the cube will have sides a, equal to 2r and volume $(2r)^3$

$= 8r^3$. The fraction occupancy of the cube obtained from the volume of one sphere $\frac{4}{3}\pi r^3$

i.e. $\dfrac{\frac{4}{3}\pi r^3}{8r^3}$ comes out to be 0.524 (or, 52.4 percent packing efficiency).

The lattice of a body centered cube (figure 5b) contains an additional point at the centre, which is exclousively belongs inside the cube. The sphere filling model shows that each cube effectively contains $8\times\frac{1}{8}+1$ or two shperes. The fraction of volume of the cube occupied by the spheres taking length of body diagonal $\left(\sqrt{3}a\right)=4r$ is calculated to be 0.680 i.e. 68 percent packing efficiency or packing efficiently = 68.

The face centred cubic lattice (figure 5c) has in addition to eight corner points, one point at the centre of each face. The sphere occupying the faces are shared between two adjacent cubes. So the unit call contains $8\times\frac{1}{8}+6\times\frac{1}{2}$, a total of 4 spheres. The size correlation between the cube edge (a) and the radius of the sphere, r; is shown in the figure 5. The face diagonal is $\sqrt{2}$ a equals to 4r. The fraction of space occupied by the spheres is 0.740. i.e., 74 percent. (percent packing efficiency=74).

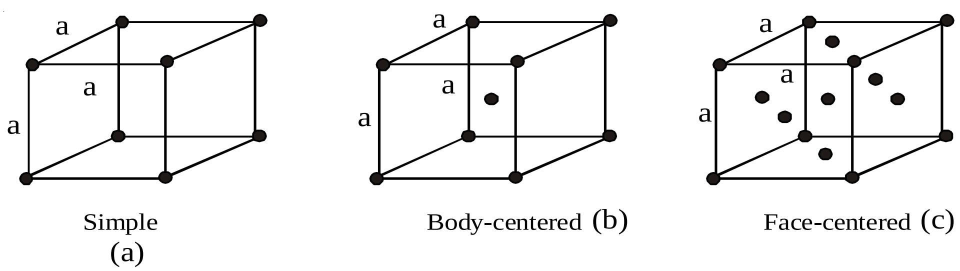


Fig. 5 : Cubic Lattice

Table 5 :

Properties of various cubic close packing of uniform sphere

		Simple Cube	**Body centred Cube**	**Face centred Cube**
a)	Volume of unit cell	a^3	a^3	a^3
b)	Lattice point per cell	8	9	14

c)	Distance of nearest neighbour touching each other	a	$\frac{\sqrt{3}a}{2}$	$a\sqrt{2}$
d)	Number of spheres per unit cell	1	2	4
e)	Fraction of volume occupied.	0.521	0.680	0.740
f)	Coordination number	6	8	12

1.9 Structure of ionic solids

Structure of some simple ionic crystal consistent with the previous study is given below with examples.

Assumptions:

i) Ions are essentially spherical.

ii) Ions are not polarised.

iii) The cation is usually smaller is size.

Formula of type AB like zinic blinde (ZnS) is close-packed face centred cubic lattice (fcc) consisting of sulphide ions occupying the lattice prints of fcc lattice and the zinc ions occupying half the tetrahedral holes.

Again as spheres give rise to 2n tetrahedral holes, any structure involving all the tetrahedral help occupied should become AB_2 type. Where B ions occupy all the tetrahedral holes provided by close packing of A ions in lattice points of a fcc lattice. This situation is found in fluorite structure (CaF_2). The fluoride ions occupy the tetrahedral holes in an fcc array of calcium ions. The position of cations and anions are interchanged in compounds of forms A_2B e.g., Na_2O, Where the sodium ions occupy all the tetrahedral holes in a close-packed fcc array of oxide ions. This structure is termed as antiflurite structure.

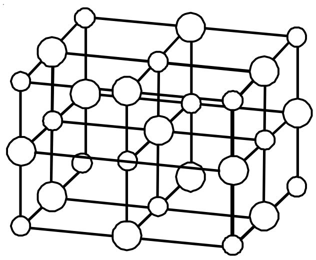
Examples of fluorite structure: CaF_2, SrF_2, BaF_2, $BaCl_2$ MO_2 (M=Zr, Hf, Ce, Th, Np, Pu). Examples of antifluorite structure: Li_2O, Na_2O etc.

The sodium chloride structure (6 : 6 coordination)

In rock salt or NaCl structure, the chloride ions form a face centred cubic lattice.

Similarly sodium ion also form an fcc lattice. The entire structure is formed by two interpenetrating fcc lattices of Na^+ and Cl^-

The structure can also be interpreted in terms of cubic close packing (ccp i.e. fcc) of Cl^- ions in which each of octahedral holes is occupied by Na^+ ions, and there is one octahedral hole per Cl^- ion. Hence in the crystal all the octahedral holes are occupied by Na^+ ions.



Larger circle O = Na^+
Smaller circle o = Cl^-

Fig. 6 NaCl structure

The unit cell has effectively 4 Na^+ and 4 Cl^- ions.

$$Na^+ = 1 \text{ (centre)} + \frac{1}{4} \times 12 \text{ (edge-centre)} = 4$$

$$Cl^- = \frac{1}{8}\times 8 \text{ (corner)} + \frac{1}{2} \times 6 \text{ (face-centre)} = 4$$

each Na^+ is surrounded by 6 Cl^- ion as nearest neighbour and vice versa.

The structure is not a closest-packed one since the ions along the diagonals of a cubic face do not touch each other.

Zinc blende or Sphalerite Structure (4 : 4 coordination number) :

In zinc blende structure 4 zinc ions and 4 sulphide ions are present per unit cell to give a cubic structure. (Disscussed previously). The fcc lattice, of S^{2-} have one octahedral hole and two tetrahedral (Td) holes per S^{2-} ion. Only half of the 8 alternate. Td holes are occupied. Examples are ZnX, CdX, HgX (X=S, Sc, Te) CuX (X=Cl, Br, I) BcS.

Wurtzite structure (4 : 4 coordination) :

Zinc sulphide also crystallises in a different way when the unit call is hexagonal, or it may be defined as half tetrahedron. Here the S^{2-} ions are in Acp array and Zn^{+2} ions occupy half of Td holes. Each ion is tetrahedrally sorrowded by the opposite ions. Examples are MgTe, CdS, AlN, BeO etc.

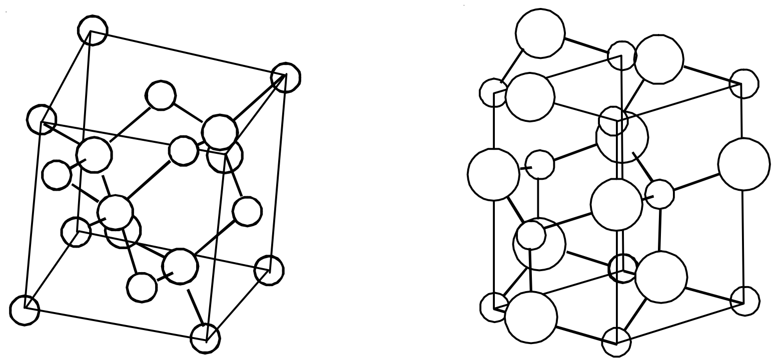


Figure 7

(a) Zinc blende cubic (b) Wurtzite Hexagonal

Fluorite structure (8 : 4 coordination) : The structure can be seen as interpenetrating simple cubic (sc) and face centred cubic (fcc) lattices of ions. The coordination numbers are 8 for cation. Eight fluoride ions form a cube about each calcium ion. Coordination number is for the anion. Four calcium ions are tetrahedrally arranged about each F^- ion. The Ca^{2+} ions are at the lattice prints of fcc lattice and all 8 Td holes are occubied by F^- ions. There are 4 Ca^{+2} ions per unit cell in which the 8 Td holes possess 8 F^- ions.

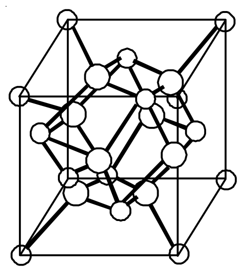


Fig. 8 : Flurite Structure

Antefluorite: If the numbers and positions of the cations and anions are reversed as in the structure of fluorite, the antefluorite structure is generated adopted by the oxides and the sulphides of Li, Na, K and Rb.

Perovskite: The mixed metal oxides with the structure of the mineral perovskite ($CaTiO_3$). The O^{2-} and Ca^{2+} ions both form ccp array in which the Oh holes formed by O^{2-} ions are occupied by smaller cations (Ti^{+4}).

General representation of perovskite structure are $A^{II}B^{IV}O_3$ (A=Ca, Sr, Ba; B=Ti, Zr, Ge, Sn) $A^{IV}B^{IV}O_3$ (A=La; B=Al, Cr. Mn, Ti), $A^{I}B^{V}O_3$ (A=Na, K; B=Nb, Ta). Mixed fluorides as $KZnF_3$, K_2NiF_4, $A^{I}NiF_4$, $A^{I}B^{II}Cl_3$ (A=Cs; B=Ca, Cd, Hg), $A^{II}B^{IV}S_3$ (A=Sr, Ba; B=Ti) also have perovskite structure. Nowadays they are of special interest. They have high temperature super conducting property such as $YBa_2Cu_3O_{7\text{-}8}$, at high temperature 100±20K, greater than the boiling point of nitrogen (77K) but much lower than normal temperature of earth. The super conductor has perouskite like structure. There are systamatic oxygen vacancies in the unit cell compared to a simple perovakite unit cell. These occur between the adjacent copper atoms in the chain along z axis. The vacancies are on the yttrium atom-plane.

Layer lattice structure (Two dimensional lattices): Ionic compounds with significant covalent character having properties between typical ionic and covolent compound, may adopt chain structures sheet structures etc.

These compounds crystalize in structures that are hard to recognize. In the structure of simple cadmium iodide the cadmium ions occupy octahedral holes in a hexagonal closed packed structure of iodide ions with helf of octahedral holes occupied by Cd but in a definite layered structure that can only be described in terms of co-valent bonding and infinite layer of molecules. A schemetic relationship in terms of size and polarisability is shown:

Increasing polarisation due to electronic configuration and cation electronegativity →

increasing polarisation due to small cation and large anion ↓		
	CaF_2	
	TiO_2	$CdCl_2$
	SiO_2	CdI_2, $HgCl_2$
	Transition metal halides.	

layared structure is seen in most of the transition metal halides which adopts $CdCl_2$ or CdI_2 structure.

CdI_2 like structure: $TiCl_2$, VCl_2, $MnCl_2$, $FeBr_2$, $CoCl_2$, PbI_2, CaI_2, TiI_2 etc.

$CdCl_2$ like structure: $MgCl_2$, $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $ZnCl_2$, $CdCl_2$, $NiBr_2$, $ZnBr_2$, NiI_2, ZnI_2 etc.

1.10 Qualitative idea about stoichiometric and nonstoichio method crystal defects:

In a crystal there occurs infinite repitition of the unit cells where the number of cations and anions are same. But there may occur some imbalances of the constituents somewhere in the crystal. Such condition is termed as lattice defect. When one or two lattice sites are missing it is called point defect. When one line is missing it is called line defect and when one plane is missing, it is called plane defect. Point defects in crystals can be of two types: (i) stoichiometric defects and (ii) non-stoichiometric defects. Stoichiometric defect also can be of two types namely Schottky and Frenkel defects. In stoichiometric defects, the ratio of the number of constituent positive and negative ions in the crystal do not change as indicated by chemical formula.

Schottky defect: Schottky defect arises from a missing cation which is accompanied by a vacancy of nearby anion site. That is a cation-anion pair is absent. Thus the electrical neutrality and the stoichiometry of the crystal is preserved, creating a pair of holes or void space.

Crystals of NaCl, KCl, KBr, $CaCl_2$ etc. exhibits Schottky defect. In NaCl crystal, missing of a Na^+ ion is accompanied by a missing Cl^- ion, while in $CaCl_2$ crystal missing of one Ca^{+2} ion is accompanied by two missing Cl^- ions.

At 130°C NaCl shows 10^6 Schottky pair per cm. The number of ions per cm^3 is about 10^{22}. So there are about one Schottky defect per 10^{16} ions.

FrenKel difect: In frenKel defect an ion gets missing from its normal site and occupies an interstitial void. Usually smaller sized cations tend to occupy interstitial sites rather than the anions. Electrical neutrality and stoichiometry of the compound is not lost. Small cations in combination with large anions, or crystals with a rather open structure exhibit this defect.

Example: AgCl, AgBr, AgI, ZnS, CaF_2.

Both Schottky and FrenKel defect may occur in a same compound like AgBr. In Schottky defect the dietectric constant of the crystallin substance is not changed significantly. But in Frenkel defect proximity of like charges (usually cation) increases the dielectric constant.

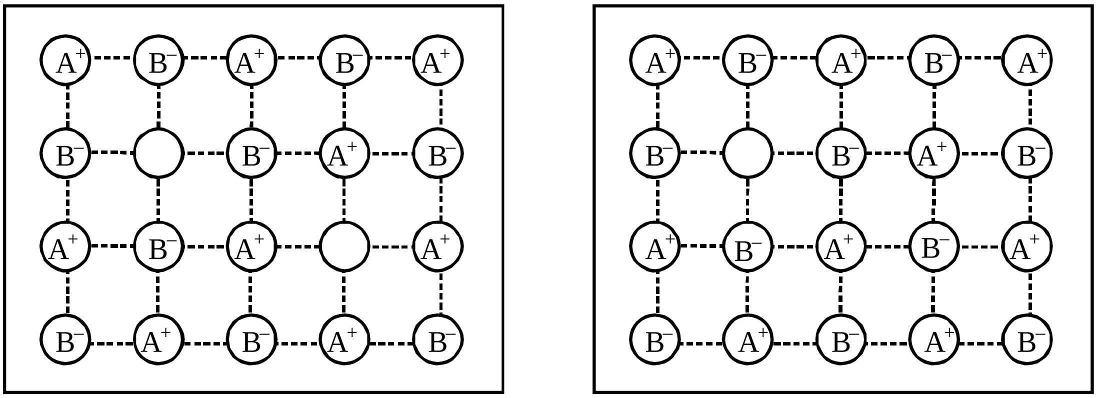


Fig. 9 Stoichiometric defects.

Non stoichiometric defects or Berthollide defect: In the compounds showing this type of defect, the ratio of positive and negative ion differ from that indicated in their representative chemical formula. The balance of –ve or +ve charge is maintained by extra electrons or positive ions as necessary.

Nonstoichiometric defect is of the main types: i) Metal excess and ii) Metal deficient.

In some cases incorporation of impurity may also show a third type.

Metal excess: Metal excess defect may occur in two ways—

i) An anion may be missing from its lattice site, an electron is present there to maintain the electroneutrality. Sodium chloride treated with sodium vapour forms this type of yellow nonstoichiometric variety.

ii) An extra metal atom may be present in an interstitial position. An electron in some other interstitial position balance the charge. Zinc Oxide enhibits this type of metal excess defect. When heated, ZnO lattice loses oxygen resulting $Z_{1+x}O$. The additional Zn ions cause lattice defect, with trapped electrons. These electrons can be excited by absorption of visible light and shows an yellow colour when hot.

Anion vacancies are created on heating the alkalimetal halides. The excess metal ions on the surface the crystal difuse inwards and ionize by crystal energy. The metal ion occupies a normal cation site where as the electron occupies an anion site Resulting compound becomes $Na_{1+x}Cl$ where x << 1. The electron trapped in anion vacancies give rise to different colours. LiCl-pink, KCl-violet, KBr-blue green, NaCl-orange. These electrons in halide ion vacancies are known as colour centres or F-centres (from German Farbenzentrum). F-centres can be generated by exposing the crystal to an X-ray beam.

Metal deficient defect :

This can occur in two ways:

i) A positive ion is absent from its lattice site, oxidation of another cation maintains the charge balance.

ii) An extra negative ion occupies an interstetial position, charge being balanced as above. There are no known examples, as large anions are difficult to fit into Interstitial positions.

This type of defect require variable valency of the cation. FeS, FeO, NiO are examples of this type (Represented as $Fe_{1-x}S$, $Fe_{1-x}O$, $Ni_{1-x}O$ etc.)

When NiO (pale green) is heated to 1500K with excess oxygen, the colour turns black and the oxide becomes scmiconductor.

The second possibility of metal deficiency by gaining an extra anion is not possible since the anoins being large, it is difficult to occupy an interstelial position by an anion as already stated above.

Nonsloichiometric defect may also occur through sustitution, when a foreign cation of comparable size replaces a cation in the lattice. A Cd^{2+} ion of comparable size to Ag^+ can replace two Ag^+ ion from a crystal of AgCl.

When a little Li_2O is dissolved in NiO, some Li^+ ion replaces Ni^{2+}. More Ni^{3+} is produced in the lattice to balance the charge of univalent Li^+ ion. This enhances the electrical conductance of the doped NiO making it a p-type semiconductor.

1.11 Summary

In this chapter the structure, energetics and properties of ionic crystals have been discussed.

Crystal Lattice: The pattern in space formed by the identical repitition of basic unit of the ionic crystalline compound.

Unit Cell: It is the smallest part of the crystal which produce, by infinite repitition in three dimentional space:

There are seven main types of unit cells—cubic, tetragonal, orthorhombic, monoclinic, hexagonal, triclinic and rhombohedral.

Cubic unit are of three types: simple cube, body centre cube and face centre cube. The rock-salt structure, Zinc-Blende structure and CsCl structure are the most common ionic structures.

Radius Ratio: Radius ratio $\frac{r_+}{r_-}$ helps to determine the coordination number and structure of a crystal.

Lattice Energy: It is the amount of energy required for complete separation of the constituent ions of the lattice to imfinity for one mole of the crystal.

Madelung Constant: It is the measure of the net electrostatic interaction of all ions in a given lattice.

Polarisation: Ionic compounds is some cases may have covalent character. This is caused by the electrostatic attraction of the charge clouds of the anion by the cations of small size.

Ionic Potential (ϕ): It is a measure of polarising power of the cation.

$$\text{Ionic Potential } (\phi) = \frac{\text{Charge of the ion}}{\text{radius of the ion}}$$

Fajan's Rules: The effect of polarization is summarised in Fajans rules.

Lattice Defect: The imperfection in the internal distribution of ions in a crystal is defined as lattice defect. The two main types of defect are i) Schottky defect ii) Frenkel defect.

1.12 Selt Assessment Questions

Unit I

Chemical bonding-I (Ionic bonds)

1. Sub unit: Lattice Energy

Q1. Establish Born-Landé equation for the formation of crystals having NaCl structure, explaining the various terms involved in it.

Q2. Calculate the lattice energy for CsI crystal for which the equilibrium inter ionic distance is 3.95Å. Madelung constant = 1.763 and Born exponent = 12.

Q3. Define lattice energy. Establish Born-Haber cycle for the formation of sodium chloride starting from metallic sodium and gaseous chlorine. State the usefulness of Born-Haber Cycle.

Q4. State the importance of Kapustinskii equation. Find the value of K in Kapustinaskii equation. [Hint: $K=0.874\ e^2\ N_A/4\pi\varepsilon_0$.

Q5. On the basis of change in the value of lattice enthalpy, comment on the products of the reaction between group I metals and dioxygen.

Sub unit 2: Polarization

Q1. What are polarising power and polarisability of ions? Explain with examples.

Q2. State Fajan's rules and state its usefulness.

Q3. Define ionic polantial.

Q4. Explain:

i) $HgCl_2$ is colourless while HgI_2 is red.

ii) Pb Cl_2 is colourless while PbI_2 is yellow.

iii) M.P. of LiCl is greater than that of LiI.

iv) AgI is much less soluble than AgCl.

Q5. State the effect of outer electronic configuration on the covalent character of ionic compounds.

Q6. Why is the melling point of CuCl (422°C) much lower than KCl (776°C).

Q7. What is meant by partial ionic character of a covalent bond? What are its consequences?

Sub unit 3: Radius ratio rule

Q1. State the role of radius ratio in the packing of ionic solids. What are its limitation?

Q2. Calculate the radius ratio for Tetrahedral, Octahedral and Cubic crystal structures.

Q3. Calculate the minimum value of r_+/r_- required for attaining coordination no. eight.

Q4. Why does KCl adopt the rock salt structure in spite of a radius ratio greater than 0.732 ?

Sub unit 4: Solvation energy

Q1. Explain the solubility trends :—

a) $MgSo_4$ > $CaSO_4$ > $BaSO_4$

b) MgOH < $Ca(OH)_2$<$Ba(OH)_2$

[large cation large anion and small cation small anion favours precipitation.]

Q2. CsF is more soluble than CsI where as LiF less soluble than LiI explain.

Q3. State the role of solvation energy in the dissolution process. What is the role of solvent molecutes in the dissolution process?

Q4. Establish a Born-Haber cycle for the process of dissolution of an ionic compound (MX). What are the factors on which the magnitude of solvation depends?

Sub unit 5 & 6: Packing of crystals and structure

Q1. Name the different types of crystal lattice for common ionic compounds.

Q2. Dapict the rock salt, wurtzite and zinc-blends structure of crystal lattice.

Q3. The radius of NH_4^+ ion (148 pm) suggests a CsCl structure for NH_4F but NH_4F adopts the wurtzite structure: Explain.

[Strong H-bonding faroms 4 : 4 coordinate]

Sub unit 7: Crystal Defects.

Q1. Name different types of crystal defects found in ionic solids. Explain with diagram.

Q2. What are semicorductors?

Q3. Define Schottky and Frenkel defects with examples.

Q4. When Ge is doped with Ga, it becomes a p-type semiconductor: Explain.

Q5. Discuss the kind of defect observed in the crystal structure of ZnO when heated., What is the consequence of heating?

1.13 Further Reading

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Unit 2 ❑ Chemical Bonding-II

Structure

Covalent Bond

2.0 Objectives

After reading the chapter you will be able to know about—

* Lewis structures of many compounds.
* Idea about formal charge and calculation

* Qualitative idea of V.B.T
* Properties of covalent bond, hybridisation and shapes of simple molecules.
* Resonance of Inorganic molecules
* Idea about V.S.EPR theory. MO theory
* Concept on Band theory, hydrogen bonding and Vander Waal's forces.

2.1 Covalent bond

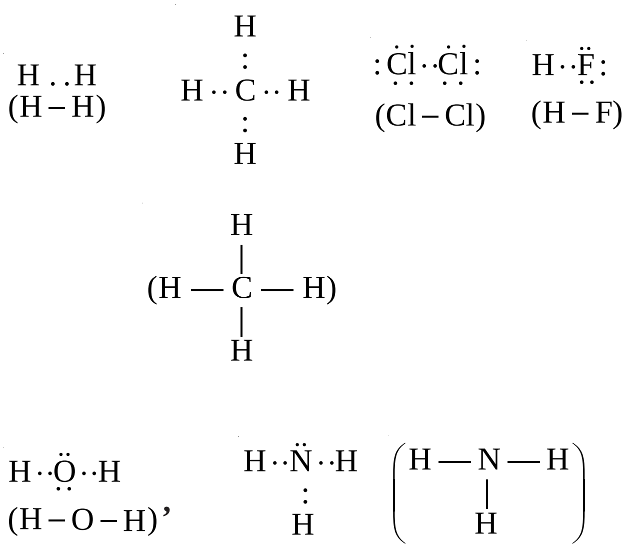
Apart from the ion formation, atoms combine with each other by sharing electrons to get an inert electronic structure (2 for hydrogen, 8 for other elements.). From Pauli exclusion principle it is obvious that 2 electrons should have to be spin paired when they occupy the same region in space (orbital) between the two nuclei (Lewis-Langmuir concept).

The bond formed by sharing electrons of two atoms is called the covalent bond, expressed by a—(line) between the aloms.

Octet rule: For most of the atoms bonded by covalent linkage, the sum of shared and unshared (lone pair) pair of electron must be eight (two for hydrogen or rule of duplet).

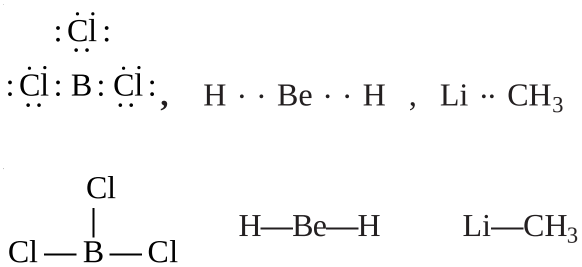
2.2 Lewis structure

The most common expression of writing the structure was first placed by G.N.Lewis. It is termed as **Lewis dot structure.**



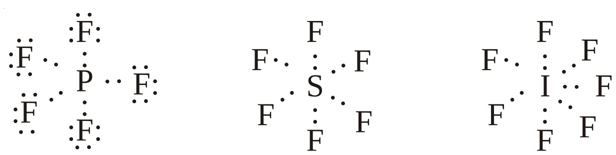
There are exceptions to the Octet rule where combining atoms have less than eight (i.e. incomplete octet) or more than eight (expansion of octet) electrons in the covalently bonded molecules.

For elements having fewer than four valence electrons, the octet will not usually be fulfilled. e.g.,



The central atom doesnot attain the octet, but the other attain octet or duplet. These compounds are referred to as electron deficient compounds.

For elements with available d-orbitals, the valence shells can be expanded beyond an octet.



PF_5 SF_6 IF_7

The central atoms have 10, 12 and 14 electrons respectively.

The molecules will seek the lowest overall energy. Maximum number of bonds and strongest possible bonds will be formed, and the arrangement of atoms in the molecule will be such so as to minimise the repulsion between the bonds, electron pairs and the nuclei.

The actual structures of the molecules are not reflected in the Lewis dot structures. The molecules are represented in a planar form.

2.3 Formal Charge

The formal charge of an atom in a Lewis dot structure of a molecule is the hypothetical charge on the atom when equal sharing of bonding electrons (constituent atoms are considered to be of same electronegativity occur and the non bonding electrons (lone pair) remain completly on the respective atoms.

The formal charge is calculated as follows:

a) Half of the electrons in all bonds to the atom under consideration = $n_{b/2}$

b) Both electrons of lone pair to the atom = n_l

c) The no. of valence electrons of the free atom = n_υ

Then Formal charge = $n_\upsilon - (n_l + n_{b/2})$

For boron atom in BF_3 : $n_\upsilon = 3$, $n_b = 6$

$n_l = 0$. Formal charge = $3 - \left(0 + \frac{6}{2}\right) = 0$

In $COCl_2$, for carbon atom, $n_\upsilon = 4$, $n_b = 8$,

$n_l = 0$. $\therefore$ Formal charge = $4 - \left(0 + \frac{1}{2} \times 8\right) = 0$

In CO_3^-, for single bonded O atom, $n_\upsilon = 6$, $n_b = 2$, $n_l = 6$. Formal charge on single bonded 'O' = $6 - \left(6 + \frac{2}{2}\right) = -1$.

For double bonded 'O' in CO_3^{2-}, $n_u = 6$, $n_b = 4$, $n_l = 4$. Formal charge = $6 - \left(4 + \frac{1}{2} \times 4\right) = 0$.

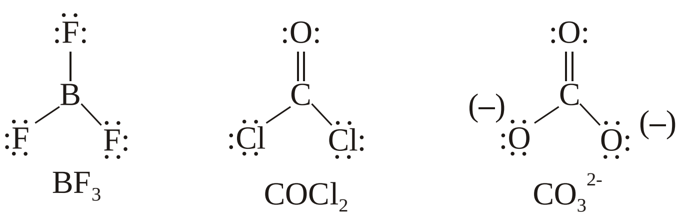


Fig. 1 Lewis structures of some molecules

2.4 Qualitative idea of Valence Bond Theory (VBT)

The basic idea of valence bond theory is the formation of the bond through spin pairing of valence electrons between the constituent atoms. The combining species approach each other from infinity and at equitibrium distance the potential energy drops to a minimum. The VBT was proposed by Heitler and London and extended by Pauling and Slater.

The simplest electron pair bond is represented in the dihydrogen molecule, H_2. To calculate the energy of a system of two hydrogen atoms, say H_A and H_B at various inter nuclear separation R_{AB}, schrödinger equation ($H\psi = E\psi$) may be applied. Now the energy (E) may be compared for different inter neuclear separation from the molecular potential energy curve. **(Fig.2)**

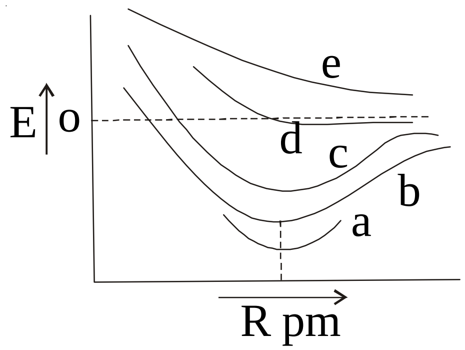


Fig 2. Theoretical energy curves for hydrogen molecule

a = experimental curve

b, c, d = compared with the experimental curve, shows successive approximation in the wave function.

e = the repulsive interaction of two electrons of like spin.

Now, ψ_A and ψ_B are the two wave functions of H-atom A and atom B. When they are sufficiently isolated that they do not interact, then the wave for the system of two atoms,

$\psi = \psi_A(1).\psi_B(2)$, electron (1) is under the control of atom A and electron (2) is under the centrol of atom B.

Now a second term may be introduced when the two electrons inter change their position. Then

$$\psi = \psi_A(1)\ \psi_B(2) + \psi_A(2).\psi_B(1)$$

Again, both the electrons may come under the influence of hydrogen atom A or under the atom B, then

$$\psi = \psi_A(1)\ \psi_B(2) + \psi_A(2)\ \psi_B(1) + \lambda\psi_A(1)\ \psi_A(2) + \lambda\psi_B(1)\ \psi_B(2).$$

The first two terms represents the covalent bond and the last two terms represent the ionic contribution of valence bond theory. Thus

$$\psi = \psi_{covalent} + \lambda\psi_{ionic}$$

where λ is a mixing coefficient. It is less probable that finding both the electrons on the same atom as they tend to repel each other. So $\lambda < 1$.

The two bonding electrons are of opposite spin. If they are of parallel spin, no bonding occurs, but there is repulsion (curve l^c, fig.2). This is a result of Pauli exclusion principle and therefore VBT is also referred to as electron pair theory.

2.5 Directional Properties of Covalent Bond

From the Lewis dot. structure, the shape of a molecule can not be determined. To arrive at an idea of shape of a molecule, the VSEPR theory, i.e., The Valence Shell Electron Pair Repulsion Theory is much useful. On the basis of minimum electrostatic repulsion between the negatively charged electrons in the valence shell of the central atom present as covalent bond pairs or lone pairs of electrons. This theory has been first proposed by Sidgwick and Powell (1940) and developed by Gillespie and Nyholm (1957). The VSEPR theory states that: All the valence shell electron pairs (bonding and nonbonding) are oriented in space arround the central atom as far apart as possible to minimise repulsion.

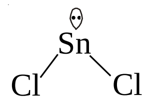
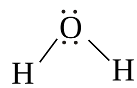
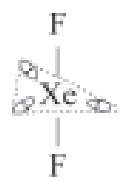
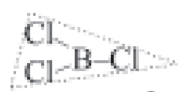
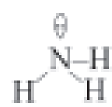
It is seen that lone pairs repel stronger than the bonded pairs as lone pairs occupy more space than bonded pairs. The repulsion order is: lone pair-lone pair > lone pair - bonded pair > bonded pair bonded pair. It is assumed that the inner electrons of the interacting atoms of the molecule do not take part in repulsion. To determine the geometry of a molecule, following steps are to be adopted:

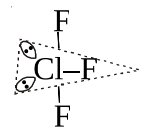
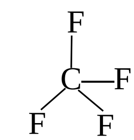
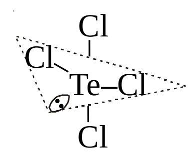
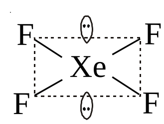
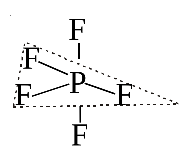
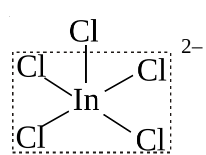
1. A reasonable Lewis structure of the molecule is to be selected.
2. Total number of lone pairs and number of atoms linked to the central atom is known, irrespective of single or multiple bonds involved in the bonding.
3. In the molecules containing lone pairs, the actual structure is determined by the position of the atoms only. Lone pairs are not included in describing the shape. But the position of the lone pairs and repulsion between the bonds is important to describe the relative positions of the atoms.

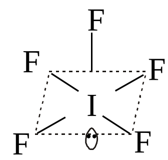
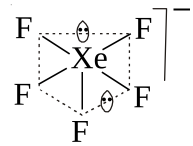
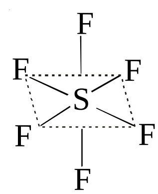
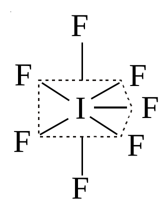
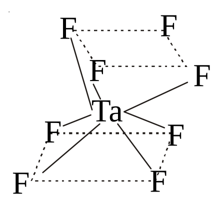
For a molecule AX_mE_n, where A = central atom, X = any other atom, E = lone pair on A, the steric number is m + n, which indicates the coordination number of **A.** The basic distribution of electron pairs in space around the central atom follows the principle of minimum repulsion. i.e., maximum angular separation as follows :

Steric no.	Arrangement	Steric no.	Arrangement
2.	linear	6.	Octahedral
3.	Triangular	7.	Pentagond bipyramid
4.	Tetrahedral	8.	Square antiprism

Table 1 : Geometry of some typical molecules (VSEPR theory)

Represen-tative formula	Type of Molecule (E=lone pair)	No. of lone pairs	S.N.	Distribu-tion of electron pairs	Shape of Molecule	Examples(s)
AX_2	AX_2	0	2	linear	linear	O=C=O $BeCl_2$, HgF_2, Zn I_2
	AX_2E	1	3	trigonal planar	bent (V-shaped)	 O_3,NO_2^-
	AX_2E_2	2	4	tetrahedral	bent (V-shaped)	 SCl_2, ClO_2^-
	AX_2E_3	3	5	trigonal bipramid	linear	 (IC_2^-, I_3^-)
AX_3	AX_3	0	3	Trigonal planar	triangular	 (NO_3^-, CO_3^{2-})
	AX_3E	1	4	tetrahedral	trigonal pyramid	 (NF_3, H_3O^+, ClO_3^-)

Representative formula	Type of Molecule (E=lone pair)	No. of lone pairs	S.N.	Distribution of electron pairs	Shape of Molecule	Examples(s)
	AX_3E_2	2	5	trigonal bipyramid	T-shape	 BrF_3
AX_4	AX_4	0	4	tetrahedral	tetrahedral	 ClO_4^-, SO_4^{2-}
	AX_4E	1	5	trigonal bipyramid	tetrahedron (irregular; sawhorse)	 SF_4
	AX_4E_2	2	6	octahedral	square planar	 ICl_4^-
AX_5	AX_5	0	5	trigonal bipyramid	trigonal bipyramid	 $PCl_5(g)$
				square[1] pyramid	square pyramid	 Ph_5Sb

Represen-tative formula	Type of Molecule (E=lone pair)	No. of lone pairs	S.N.	Distribu-tion of electron pairs	Shape of Molecule	Examples(s)
	AX_5E	1	6	octahedral	square pyramid	 (BrF_5, $XeOF_4$, TeF_5^-)
	AX_5E_2	2	7	pentagonal planar	pentagonal bipyramid	
AX_6	AX_6	0	6	octahedral	octahedral	 PCl_6^-
AX_7	AX_7	0	7	pentagonal bipyramid		
AX_8	AX_8	0	8	square antiprism		 IF_8^-

The refinement of bond angles due to repulsion of lone pairs and bond pairs is governed by certain rules.

Rule I : The number of a bonding pairs will determine the ideal geometry of the species, π-bonding pair will not influence the geometry of the system. The geometry of the molecular species with no lone pairs surrounding the central atom will be determined only by the number of a bonding electron pairs as depicted in Table 1.

When the substituents are different in electronegativity as CH_2F_2, PCl_3F_2, $COCl_2$, POF_3 etc. the bond angle changes from regular geometry and can be explained by Bent's rule.

Rule II : When central atom bears both bond pairs (b.p.) and lone pairs (l.p.), the structures deviate from regular geometries predicted from Rule I due to difference in the extent of repulsion of the electron pairs. The order of repulsion varies as: lone pair-lone pair (l.p.-l.p)>> lone pair-bond pair (l.p.-b.p.)>> bond pair-bond pair (b.p.-b.p.).

Rule III : The b.p.-b.p. repulsion decreases as the electronegativity of B atom increases in a AB_n type species where A is the central atom and n is the number of B atoms attached to A. This can be stated as BAB bond angle decreases with increasing electronegativity of B.

Rule IV : Multiple bonds do not grossly influence the geometry of a molecular species. Since multiple bonds (σ bonds alongwith π bonds) accupy more space around central atom than simple σ bonds, they create more repulsions than single σ bonds. The magnitude of repulsion follows the sequence multiple bond-multiple bond > multiple bond σ bond > σ bond-σ bond.

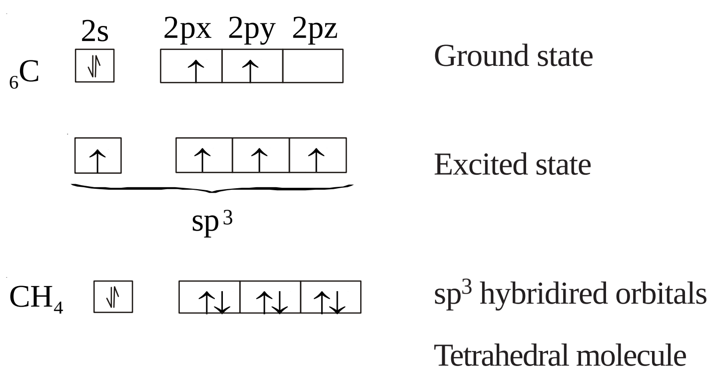
Rule V : Any repulsive force (l.p.-l.p. or b.p.-b.p.) to contract the bond angle is more singnificant for the incompletely filled valence shell compared to the completely filled valence shell. For incompletely filled shells, the deviation of bond angle from ideal behaviour is more due to greater flexibility of bonds as these is more space available for central atom compared to filled shells which have greater rigidity of bonds.

2.6 Concept of equivalent and non-equivalent hybridisation and shapes of simple molecules and ions.

The formation of a covalent lond involves the concept of overlap between atomic orbitals of combinding atoms. Atonic orbitals have definite shape in space (except s-orbital) and so overlap of atomic orbitals must occur in definite direction, and therefore covalent bond must have a directional nature. The directional nature of the covalent bond is a direct consequence of orbital overlap. The resulting covalent bonds will produce a definite geometry of each covalent molecule.

It is known that the four C—H bonds in methane are all alike and they are arranged symmetrically around the central carbon atom directed along the four corners of tetrahedron. This leads to the idea of mixing of 2s and 2p orbitals of carbon before overlap. This is called hybridization. Hybridization is a theoretical concept of mixing different atomic orbitals of comparable energy to produce equal number of orbitals of mixed character. The geometry of covalent molecules may be established by different factors: (a) Hybridisation is introduced in VBT to explain the number of bonds formed, equivalence of bonds (with exceptions), the geometry of the molecules, and better overlap of atomic orbitals. (b) Mutual repulsion of bonding electron pairs so as to make the covalent bonds as far apart as posible. (c) Repulsion between non-bonding or unshared pair of electrons greatly influence the geometry of a molecule.

The case of methane may be explained. Carbon atom has four valence shell electrons, two paired in 2s orbital and 2 unpaired in 2p orbital. To form four bonds, the two paired electron are to be unpaired first then one of them is to be promoted to the 2p orbital, which can be represented as:



Methane is tetrahedral and the bonded pair of electrons are as tas apart as possible. So the energy of the system is minimum. Hybridisation is a process by which pure atomic orbitals will redistribute their energies among themselves so as to make equivalent bonds, before combining with other atoms.

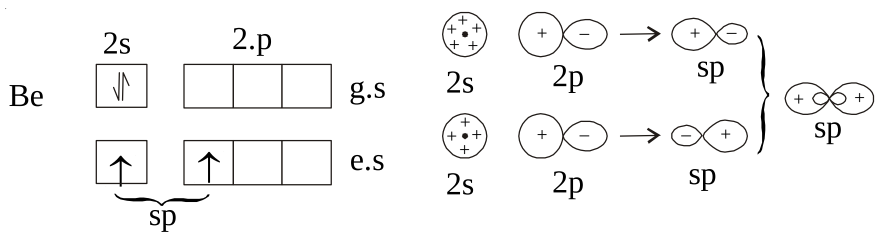
Common hybridization schemes:

Interacting orbits	Hybrid orbital	Resulting geometry
ns, np_z	sp	linear
s, p_x, p_y	sp^2	Triangular planar (XY plane)
s, px, py, pz	sp^3	Tetrahedral (Td)
(n–1)d, ns, np_x, np_y	dsp^2 or sp^2d	Square planar (xy plane)
ns, np_x, np_y, np_z, nd_{z^2}	sp^3d	Trigonal bipyramidal (TBP)
ns, np_x, np_y, np_z, $nd_{x^2-y^2}$, nd_{z^2}	sp^3d^2 or d^2sp^3	Octahedral (Oh)
ns, np_x, np_y, np_z, $nd_{x^2-y^2}$, nd_{z^2}, nd_{z^2}	d^3sp^3 or sp^3d^3	Pentagonal-bipyramidal

Some examples:

sp hybridization:

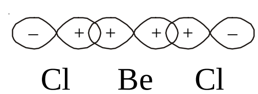
$BeCl_2$



gs = ground state

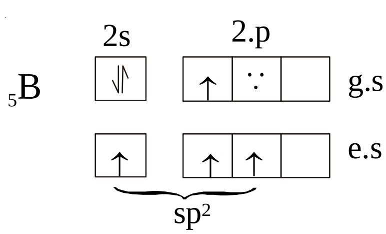
es = excited state

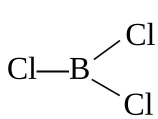
$BeCl_2$



sp^2 hybridization

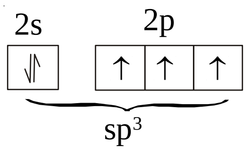
BCl_3



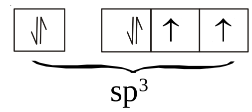


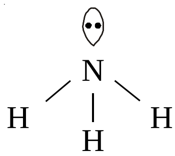
sp^3 hybridization NH_3, H_2O

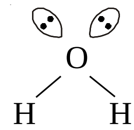
$_7N$



$_6O$





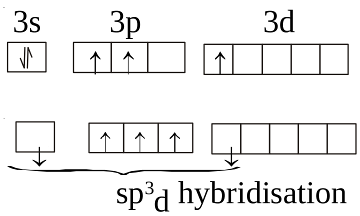


Tetrahedral including
lone pair of electron

Tetrahedral including
two lone pairs of electrons

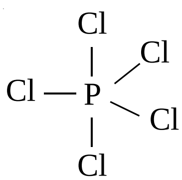
sp^3d hybridization : PCl_5, PCl_3F_2

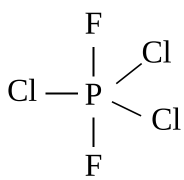
$_{15}P$



ground state

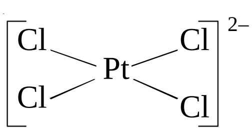
excited state





more electronegative atoms always
occupy the axial position (Bent's Rule)

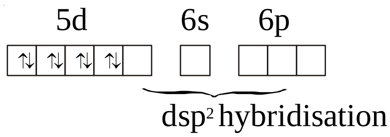
dsp^2 hybridization: $PtCl_4^{2-}$



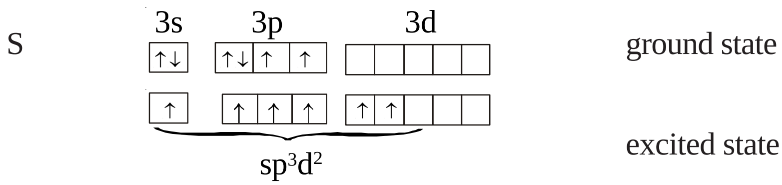
Square planar

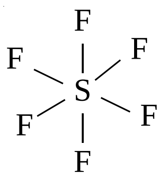
Pt : Outer electronic configuration : $5d^9\ 6S^1$

Pt^{+2} : $5d^8\ 6S^0$

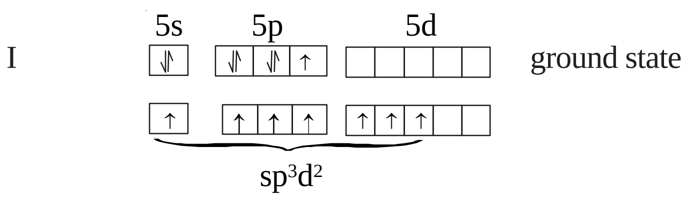


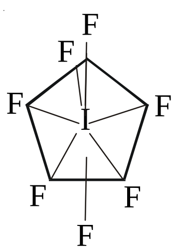
sp^3d^2 hybridization: SF_6





sp^3d^3 hybridization: IF_7





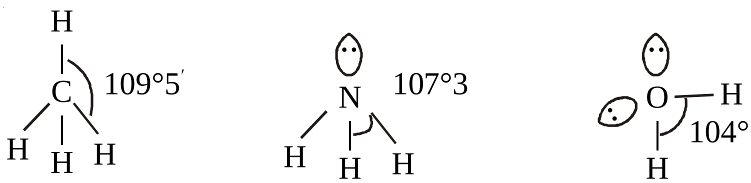
pentagonal bipyramid

The concept of hybridization was first introduced to explain the equivalence of the four bonds of CH_4. Each of the four sp^3 hybrid orbitals of carbon contain 25%S character and 75% p character and are distributed along the four corners of a regular tetrahedron. When there is no lone pair of electron on the central atom then the situation is ideal and all bonds are equivalent. When lone pair of electron is present on the central atom, then the situation of s : p ratio of the sp^3 hybrid change from ideal ratio. In NH_3 and H_2O there are one and two lone pairs respectively on the central atom. These hybrid orbitals become non-equivalent hybrid orbitals but still called sp^3 hybrid orbitals.

Now it was seen that in some molecules like CH_3F, CH_3Cl the bond lengths and bond angles differ from the ideal situation:

Molecule	**Bond**	**length**	**Molecule**	**Bond**	**length**
CH_3F	C—F	139.1 pm	CF_4	C—F	132.3 pm
CH_3Cl	C—Cl	170.3 pm	CH_2Cl_2	C—Cl	177.2 pm
CF_3Cl	C—Cl	175 pm	$CHCl_3$	C—Cl	176.4 pm
C_2H_6	C—C	153.6 pm	CCl_4	C—Cl	176.4 pm
C_2F_6	C—C	151 pm			

The effect of lone pairs on bonds angles is manifested in the following molecules. The tetrahedral bond angle in methane is 109°5', in ammonia the angle becomes 107° and in water it is further reduced to 104°.



CH_4 NH_3 H_2O

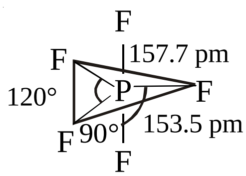
In trigonal bipyramidal structure there are two positions to accomodate the lone pair. One in the axial position with nearest bond angle 90° and other in the equitorial position the bond angle is 120°. Therefore the lone pair always prefer the equitorial position, where the repulsion is minimised. There are some special cases, such as in NH_3 < HNH bond angle is 107°C whereas in NF_3 ∠ HFH bond angle is 102°. As the bonded atom is more electronegative, bond pair is displaced further from the central atom, and so bp - bp repulsion decreases.

In NH_3 ∠ HNH = 107°3'

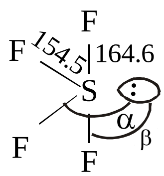
and in PH_3 ∠ HPH = 93°3'

Compaired to the 1st period elements, the 2nd period element are larger and the repulsion between lp - bp dominates. In CH_2F_2 ∠ HCH is 111.9°, whereas ∠FCF is 108°3, which suggests less than 25% s character is C—F bond. In the sp^3d^2 and sp^3d

hybridisation, there are two sets of orbitals shown in the structures below. In structure (a) and (b) sp^3d i.e. trigonal bipyramid structure, one set is sp^2 oriented in the equitorial position and pd oriented along the vertical position. In the equitorial plane, the orbitals are rich in s-character so the bond lengths are shorter and axial that is vertical bonds are relatively longer.



(a)



(b)

α = 129.3

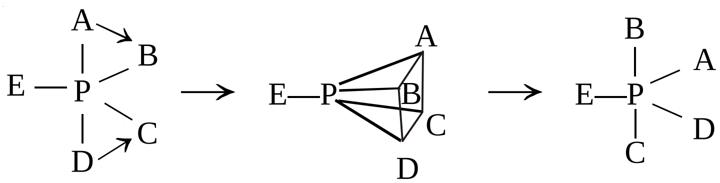
β = 93.5

The lone pair will always occupy the equitorial position. In compounds like PCl_2F_3, PCl_3F_2 etc. the more electronegative elements will occupy the axial position. (Bent's section 2.9)

2.7 Stereochemically non-rigid molecules Berry's pseudorotation

The structures predicted by VSEPR and Bent's rule are structurally rigid or static molecular species. However, there are many molecules which are structurally non-rigid or stereochemically non-rigid. If the rearrangement of structures of a molecule gives configulation which are chemically equivalent having minimum energy and are easily transformed from one form to other, the molecule is said to be 'fluxional'. Fluxional molecules differ from other stareochemically non-rigid molecules in possessing more than a single configuration with minimum energy.

Berry's pseudorotation: The structure of PCl_2F_3 will have two Fatoms in axial position and two Cl and one F atom in equatorial position according to Bent's Rule (section 2.9) in a TBP geometry. But NMR studies at various temperatures reveal that all Fatoms are equivalent and undergo structural change which is consistent with the time scale of NMR experiment. Interchange of axial and equitorial groups in a trigonal bipyramid (TBP) structure may occur therefore, in some cases. The mechanism was suggested by R.S. Berry and is known as Berry pseudorotation. In a molecule of AX_5 type, without any lone pair on A, the structure is TBP corresponding to sp^3d hybridisation of the central atom which is not energetically favoured in many cases. Accordingly, a TBP structure may readily convert to a square pyramid structure and then back back to a new TBP structure.



The two axial groups interchange with two equatorial groups while the third equatorial group (taken as pivotgroup) remains unchanged in both configurations.

The whole molecule has undergone a rotation about an axis around E and the central atom. Many phosphorus compoundes show Berry pseudo-rotation.

CH_3PF_4 can interchange axial and equitorial fluorine atoms by rotation about P—CH_3 axis. In $(CH_3)_2$ PF_3, the electropositive CH_3 group may come to the axial position in the new TBP. This process involves high energy, and so the equitorial CH_3 groups will not change place.

2.8 Resonance of Inorganic Molecules

From Valence Bond Theory a theoretical mechanism is obtained to explain the stability and other properties of a polynuclear molecule which can not be explained by any single electron dot structure. As in H_2 molecule, the following structures are said to be in resonance. (1,2 are electrons attached to H_A and H_B respectively)

$$H_A^1 H_B^2 \leftrightarrow H_A^2 H_B^1 \leftrightarrow \overset{1,2}{H_A^-} H_B^+ \leftrightarrow H_B^+ \overset{1,2}{H_B^-}$$

(I) (II) (III) (IV)

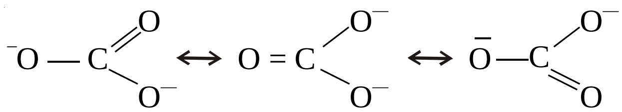
The wave function corresponding to each hypothetical structure by suitable energy equation to get the energy of H_2 molecule is lower than the energy of any of the resonating structures. Thus the true structure of H_2 molecule is not represented by any of the three structures, but a mixture or a resonance hybrod of all the structures. The energy of 'resonance hybrid' is lower than the energy of any of the contributing structures. The phe3nomenor is known as resonance and the molecule is said to have resonance forms. Thus the actual wave function of a resonance hybrid can be represented by the linear combination of individual wave functions of each structure i.e. $\psi = C_1\psi_1 + C_2\psi_2 + ...$ The different structures are known as canonical structures. The actual structure is more stable than any of canonical forms and this extra stability is known as resonanse energy.

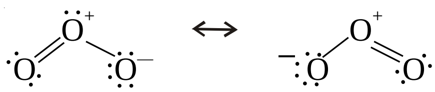
Resonance structures of some morganic molecules are given below:

i) CO $C=O \leftrightarrow {}^{-}C \cong O^{+} \leftrightarrow {}^{+}C-O^{-}$

$:C::\ddot{O} \leftrightarrow {}^{-}C:::O^{+}: \leftrightarrow :C^{+}:O:^{-}$

Resonance energy is: (the observed heat of formation — The calculated heat of formation.)

ii) $CO_3^{=}$:  and soon.

iii) Ozone: 

The necessary conditions for resonane hybrid structures are:

1. The atomic skeleton of the molecules must not be changed, i.e. the atoms must have same position is canonical forms. e.g. N—N—O and N—O—N can not be present in the same resonating hybrid. (So tautomers cannot be treated as resonating structures).
2. The number of unpaired electrons must be the same in all the contributing structures.
3. Only those structures will contribute which possess similar energies in the resonance hybrid. The more electronegative element will not carry a positive charge. Thus $^{2-}:\ddot{N}—\overset{+}{N}=\overset{+}{O}:$ is not a canonical form of N_2O molecule.
4. Canonical forms with adjacent like charges are unfavourable. as $A^-–B^+–C^+–D^-$ structure is unfavourable, whereas adjacent charges of opposite sign will be more favourable than when the charges are separated. So, in case of undissociated hydrazoic acid, structure (II) contributed less compared to the structures (I) and (III).

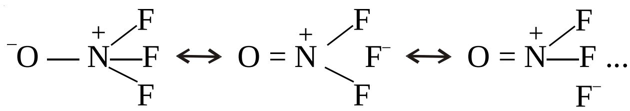
$$\underset{(I)}{H-N=\overset{+}{N}=N^-} \leftrightarrow \underset{(II)}{H-N^+\equiv N^+-N^{2-}} \leftrightarrow \underset{(III)}{H-N^--N^+\equiv N}$$

No Bond Resonane:

There is another kind of resonance where one species may not be bonded with the rest of the molecule. This is called hyperconjugation of no bond resonance.

$$A - X - B \leftrightarrow A^{+} = X \; B^{-}$$

As in ONF_3



In tautomerism such as keto-enol tautomerism arrangement of atoms change but in Resonance atoms will not change their relative position in the molecule.

2.9 Dipole moments of inorganic molecules and ions

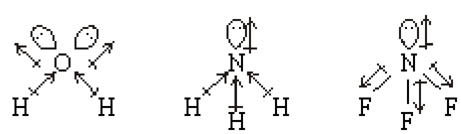
The covalent bond between two atoms of the same element is shared equally by the two nuclei concerned. But for bonds between atoms of two different elements, the bonding electrons are not equally distributed between the two nuclei. The electron pair will be shifted towards the more electronagative element. The bond thus gets polar. The polarity is expressed in terms of electric dipole moment vector μ.

$$\mu = q.d. \text{ (coulomb metre) } q^{+} \underset{d}{\xrightarrow{+\quad}} .q^{-}$$

q^+ and q^- are charges on the atoms sparated by a distance d. [SI unit is coulomb metre, common unit debye].

1 Debye = 10^{-8} esu.cm = $3.33564.10^{-30}$ coulomb metre. In a symetrical heteronuclei molecule bond moments are cancelled (O=C=O) i.e. $\mu = 0$, where as SO_2 is angular and possesses a positive dipole moment.

Lone pairs of electrons also hive some effect on dipole moment.



2.10 VSEPR Theory, Bent's rule and their applications

It is seen that the bonding of an electronegative atom or group favours to bind to orbitals having more p-character (or less s-character). The s-orbitals, with greater penetration into inner electron core faces higher effective nuclear charge of the central atom form bonds with less electronegative atoms or groups, whereas electronegative atoms or groups form bonds with orbitals having less s-character (i.e. more p-character). The mismatch of energy results in poor overlap of orbitals. These are summarised in Bent's rules proposed by H.A. Bent in 1960.

i) More electronegative substituents prefer hybrid orbitals of the central atom with greater p-character and less s-character and more electropositive substituents prefer hybrid orbitals having more s-character.

ii) The central atom involves hybrid orbitals with higher s-character to develop higher covalence, and less s-charactger in bonds with greater ionic character.

iii) The central atom will direct less p-character and greater s-character into the hybrids directed towards less electronegative substituents.

In PCl_3F_2, $PF_4(CH_3)$, $PF_3(CH_3)_2$, the fluorine atoms always occupy the axial position. Again the s-rich covalent bonds require a larger angular volume and leads to widening of bond angle. The Bent's rule gives us an idea about the refinements of bond angle over the VSEPR theory. In TBP PCl_3F_2 molecule for example, the hybridisation is sp^3d which can be considered as a combination of sp^2 and pd hybridisation (sp_xp_y lie in the xy equatorial plane and $p_zd_{z^2}$ directed mutually 180° in the axial directions i.e. perpendicular to the equational plane). The equatorial bonds have s-orbital contribution but axial bonds do not have any s-character. The more electronegative atoms will occupy axial bonds with no s-character, and chlorine atoms will accupy equational positions where the hybrid orbitals are sp^2. For sp hybrid orbitals where s and p-character are equal (50%–50%), the bond angle is 180°, for sp^2 (s-character $33\frac{1}{3}\%$, p-character $66\frac{2}{3}\%$) bond angle is 120°, and sp^3 (s-character 25% – p-character 75%) angle is 109°28', for p^2 (100% p-character) angle is 90°. The greater the s-character greater is the bond angle while greater p-character indicates smaller bond angle.

2.11 Molecular Orbital Theory (MOT)

Certain observations of the properties of molecules cannot be adequately explained by VBT. For example, oxygen molecule $:\ddot{O}=\ddot{O}:$ should be diamagnetic with each oxygen atom sp-hybridied. Experimentally it is observed that O_2 molecule is paramagnetic with two unpaired electrons. Same is true for B_2 molecule which should be diamagnetic according to VBT, but actually the molecule is paramagnetic. Such inadequacies have been taken care of in the MOT where the orbitals of the molecule are molecular orbitals and not atomic orbitals as per VBT. VBT uses hybridisation concept to describe the shapes of molecules, but the hybridised orbitals are still atomic orbitals. Each electron in a molecule is described by a certain wave function ψ which represents the orbit of the electron in a molecule, and is called molecular orbital.

When two individual hydrogen atoms comes closer and closer from a very large distance from each other, the nucleus of each atom will start to attract the electrons originally associated solely with the other atom. The change in energy of the system as a function of distance shown is in the following curve (known as Morse Curve). When the distance of separation of the nuclei is near the bonding range, two electrons in the system are both associated with the two nuclei. The original atomic orbitals on the two atom will be associated to one molecular orbital. Thus a molecular orbital is formed from the combination of two atomic orbitals.

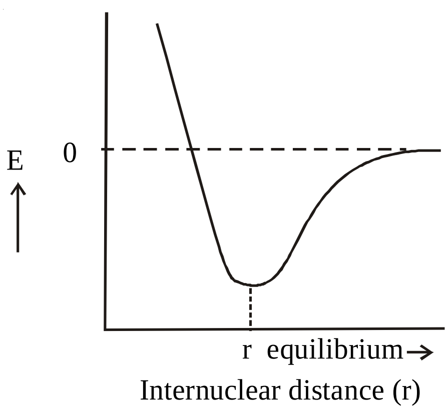


Fig. 3. The Morse Curve for Hydrogen Molecule

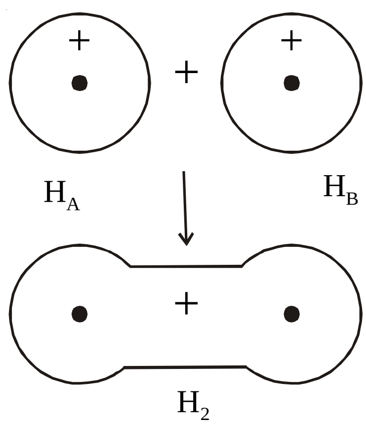


Fig. 4. Addition of two 1s atomic orbitals

The molecular orbital thus formed, is a result of linear combination of atomic orbitals. When one atom has the wave function ϕ_A and the other atom possess wave function ϕ_B

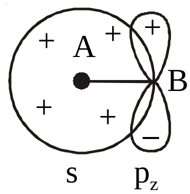
In this case the linear combination (like simple addition or subtraction) of atomic orbitals (LCAO) will produce the molecular orbital wave function ψ_{MO}.

$\psi^b_{MO} = \phi_A + \phi_B$ and $\psi^a_{MO} = \phi_A - \phi_B$ (b = bonding, a = antibonding)

For effective combination of ϕ_A and ϕ_B the following conditions should be maintained:

i) The energies of ϕ_A and ϕ_B should be of comparable magnitude. This is called energy condition and therefore best combination will occur between 1s and 1s, 3p and 3p etc. but combination between 1s and 5s, 3p and 5p will be less probable.

ii) ϕ_A and ϕ_B should have the same symmetry relation to the molecular axis of molecule AB. So s-type atomic orbital will not combine with pz type orbital if x is the molecular axis.



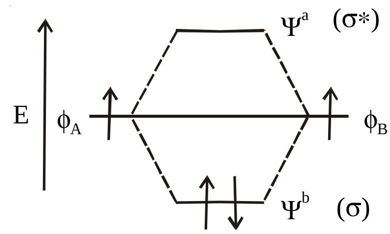
(Non-bonding condition)

iii) ϕ_A and ϕ_B should overlap one another as much as possible so that overlap integral $S_{AB} = \int \phi_A\phi_B d\tau$ and resonance integral $H_{AB} = \int \phi_A H \phi_B d\tau$ will have maximum value.

ψ^b_{MO} implies that the two electrons in the hydrogen molecule are now shared with both nuclei; that is the MO is bicentric. The MO helps to bond the two hydrogen atoms together (b indicates the bonding MO). The plus sign in the MO (Fig 4) indicates that the wave function is positive everywhere. Atomic orbitals with same sign will combine to form bonding orbital. There will be no node. (Node is the space where there is minimum probability of finding an electron).

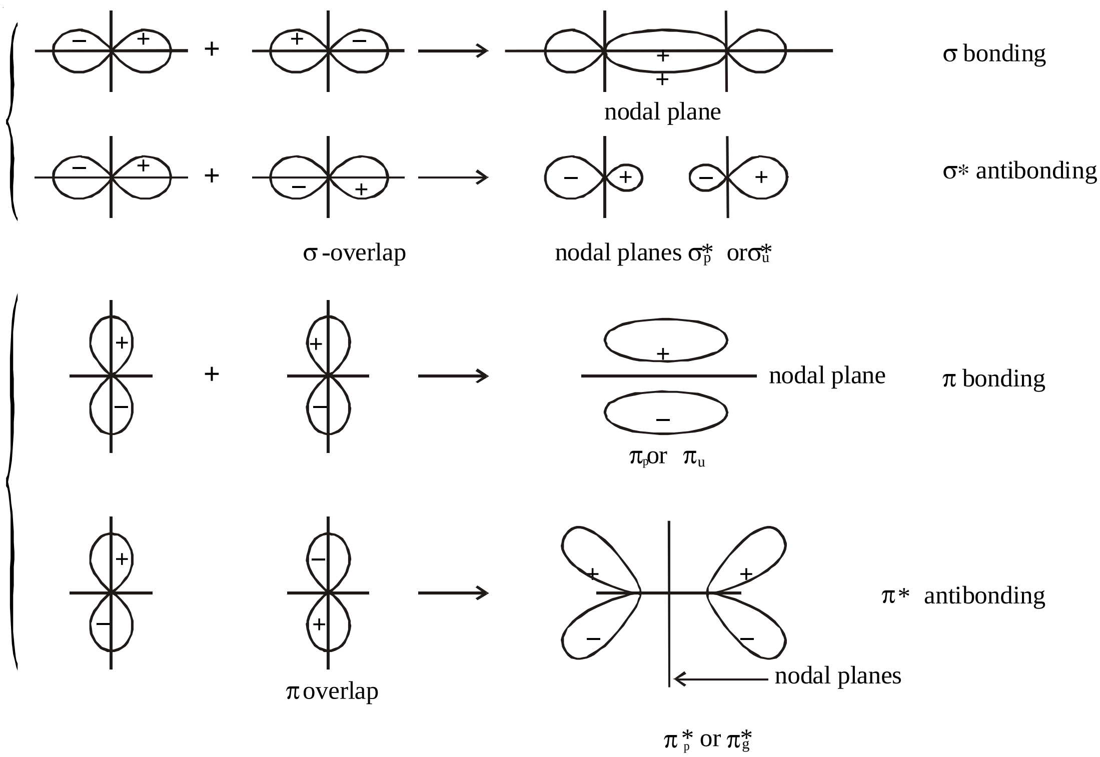
In ψ^a_{MO} ('a' stands for antibonding orbitals) which is produced from $\phi_A - \phi_B$, the probability of finding the electrons at exactly half the distance between the nuclei is zero. There is a nodal plane in the M.O.

The LCAO of atomic orbitals may be represented by an energy level diagram.



MO energy diagram of H_2

The energy of the bonding MO orbital is lower than the energies of the atomic orbitals and the energy of antibonding orbital is higher than the atomic orbitals. The bonding MO represents a σ-bonding orbital and the antibonding MO is a σ* antibonding orbital. Two p orbitals in the similar manner can form bonding orbitals, but there may be two types of overlap.



Essential features of MOT

1. Molecular orbitals are formed by the combination of atomic orbitals of individual atoms according to LCAO. The number of molecular orbitals will be equal to the combining atomic orbitals. The combining atomic orbitals must satisfy three conditions to form MO, i.e. energy, overlap and symmetry.

2. An atomic orbital is represented by a wave function. The waves have positive (crest) or negative (trough) phases or amplitude. Two waves may combine constructively (where the wave functions combine with same sign and resultant wave has enhanced amplitude) or destructively (where the wave functions have opposite sign and resultant wave has a reduced amplitude). Therefore, when two atomic orbitals undergo in phase or similar phase addition, the electron density in

between the nuclei increases and a bonding MO results whose energy is lower than the combining atomic orbitals. On the other hand, when the two wave functions combine out of phase (destructively), the electron density in between the nuclei decreases and an antibonding MO is formed which has a higher energy than the combining atomic orbitals. Thus two atomic orbitals combine to form two molecular orbitals—one bonding and the other antibonding.

3. Inner orbitals will not take best in the formation of molecular orbitals as they have smaller radii and do not overlap well with the orbitals of adjacent atoms.

4. The MO's are filled up with electrons following similar rules for filling up of atomic orbitals:

   (a) Each MO will have a maximum of two electrons (Pauli's exclusion principle)

   (b) The lower energy MO will be filled up prior to that of higher energy (Aufbau principle).

   (c) In case of degenerate MO's the electrons remain unpaired as far as possible (Hund's rule of maximum multiplicity).

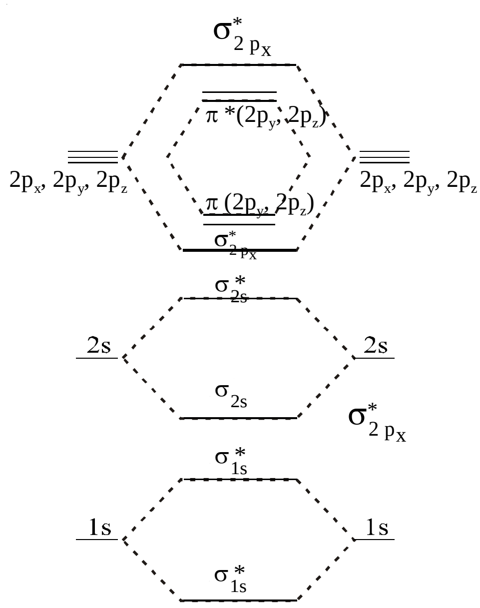


Fig. 6 MO diagram for homoneuclear diatomic molecules of second period (x-axis is the molecular axis)

Number 1,2,3 can preceed the symmetry symbol which put the MOS of that particular symmetry in ascending energy order So $\sigma_{1s} = 1\sigma_g$, $\sigma^*_{1s} = 2\sigma_u$, $\sigma_{2s} = 2\sigma_g$, $\pi_{2p} = 1\pi_u$ etc. Some of the combinatins of atomic orbitals are shown in Fig. 5. Those orbitals which are cylidrically symmetrical about the internucleai axis are called σ orbitals, (analogous to s-orbitals). If the internuclear axis lies in a nodal plane, a π bond results. The bonding and antibonding MO arises due to ± sign in LCAO i.e. $\phi_A \pm \phi_B$. $\phi_A+\phi_B$ is a bonding combination and $\phi_A-\phi_B$ is an antibonding combination. All antibonding orbitals possess an additional nodal plane perpendicular to the internuclear axis and lying between the nuclei. In addition, the molecular orbitals may or may not have a centre of symmetry. The subscript 'g' (gerade or even) and 'u' (ungerade or odd) is applied to MOs for a symmetry symbol when the molecule has a centre of symmetry. If a wave function remain unchanged in appearance under the operation of inversion, then it is of 'g' type, if it changes sign then it is 'u' type. σ-bonding MO is desigrated as σ_g, σ* as σ^*_u, π as π_u and π* as π^*_9.

Using Fig. 6 as a guide, we can proceed to build up electronic configurations of various diatomic molecules following the rules for filling up of electrons in MOs. The molecular electronic configurates of homoatonic molecules:

(i) $H_2 = \sigma_{1s}{}^2$ (2 electrons) (ii) $He_2 = \sigma_{1s}{}^2\, \sigma^{*2}_{1s}$ (4 electrons)

(iii) $Li_2 = KK\sigma^2_{2s}$ (K stands for K (1s) shell where there is no net bonding).

(iv) $Be_2 = KK\sigma^2_{2s}\ \sigma^{*2}_{2s}$

(v) O_2, F_2, Ne_2 : These three molecules can be treated with the energy diagram depicted in Fig. 6. (B_2, C_2, N_2 require additional considerations).

O_2 : $KK\sigma^2_{2s}\ \sigma^{*2}_{2s}\ \sigma_p{}^2\ \pi_{2p}{}^4\ \pi^{*2}_{2p}$ (16 electrons). But π^*_{2p} orbital (i.e. $\pi^2{}_{2py,}\ 2p_{z)}$ is doubly degenerate and Hund's rule predicts that the two electrons entering π^* level will occupy two different orbitals, and so the electronic configuration of O_2 can be written as

$O_2 = KK\sigma^2_{2s}\,\sigma^{*2}_{2s}\,\sigma^2_{2p}\,\pi^4_{2p}\,\pi^{*1}_{2py}\,\pi^{*1}_{2pz}$. [$O_2$ molecule therefore should be paramagnetic, contrary to conclusions from VBT].

F_2 : $KK\sigma^2_{2s}\ \sigma^{*2}_{2s}\ \sigma_{2p}{}^2\ \pi^4_{2p}\ \pi^{*4}_{2p}$ (18 electrons)

Ne_2 : $KK\sigma^2_{2s}\ \sigma^{*2}_{2s}\ \sigma^2_{2p}\ \pi^2_{2p}\ \pi^{*4}_{2p}\ \sigma^{*2}_{2p}$ (20 electrons)

(vi) B_2, C_2, N_2 : Following Fig. 6, B_2 molecule would be predicted to have a single σ bond (see Bond order) and diamagnetic. Experimeutally B_2 molecule is found to have 2 unpaired electrons. On the other hand, C_2 molecule would be predicted to be paramagnetic. Experiencetally, C_2 in ground state is diamagnetic.

Let us consider Fig. 6 where mixing was allowed only between orbitals on the atoms that were identical in energy. Actually, mixing will take place between all orbitals of proper symmetry, inhibited only by energy mismatch. So there will be no effective mixing of 1s and 2s orbitals (symmetry matches, but energy difference is high). The energy difference between 2s and 2p orbitals is less and varies with the effective nuclear charge. With large Zeff as in fluorine, the energy difference is high and mixing can be neglected. The difference in energy between the 2s and 2p levels increases from about 200 KJ mole^{-1} in Lithium atom to about 2500 KJ mol^{-1} in fluorine. The lower effective nuclear charge allows the 2s and 2p orbitals to come sufficiently close to mix and is equivalent to hybridisation in VBT. Another way to view this phenomenon is to ignore s-p mixing in the initial construction of MO diagram, but then recognise that MOs of the same symmetry will interact if they are close enough in energy. Thus σ_g (2s) and σ_g(2p) MOs in a molecule as B_2 will mix. As a result, the lower energy orbital [σ_g(2s)] will be stabilised and higher energy [σ_g (2p)] will become less stable. This leads to reversal in the energy ordering of the π_u (2p) and σ_g (2p) MOs [Figure 7] compared to MOs where no mixing occurs [Figure 6]. There will be some interaction between σ_u^* (2s) and σ_u^* (2p) orbitals. However, these orbitals are not close enough in energy and the interaction will be negligible. So, in Fig. 7, it is not appropriate to designate MOs as σ_g (2s) or σ_g (2p) etc. to identify their origin. So the MOs are labelled according to their symmetry and number them in order from most to the least stable.

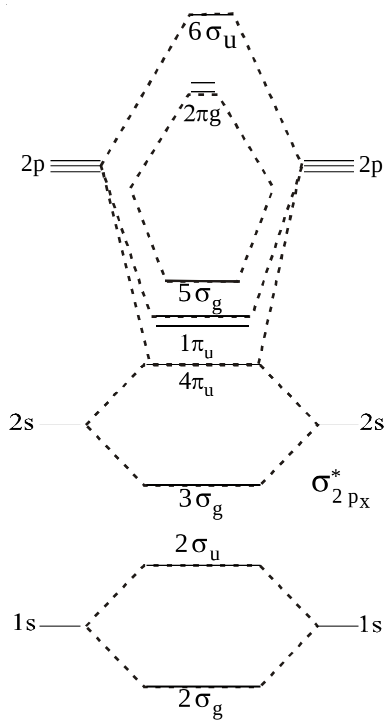


Figure 7 : Correct MO energy levels for B_2, C_2 and N_2.

The magnetic properties of B_2 and C_2 provide strong experimental verification that their electronic configurations are based on Figure 7 rather than on Figure 6.

B_2 : $KK3\sigma_g^2\ 4\sigma_u^2\ 1\pi_u^2$ (unpaired)

C_2 : $KK3\sigma_g^2\ 4\sigma_u^2\ 1\pi_u^4$ (all paired)

For N_2 (14 electrons) either diagram would give a bond order of 3 and diamagnetism. Experimental evidence supporting one configuration over the other for N_2 has been sought in photoelectron spectroscopy. The photoelectron spectrum (the method involves ionising electrons in a molecule or atom by subjecting them to radiation of appropriatge energy) of N_2 shows the orbital energies of –15.6 and –16.7 ev for $5\sigma_g$ and $1\pi_u$ respectively. So s–p mixing (or MO interaction) occurs in this molecule to make $5\sigma_g$ higher in energy than $1\pi_u$.

N_2 : $KK3\sigma_g^2\ 4\sigma_u^2\ 1\pi_u^4\ 5\sigma_g^2$.

2.12 Bond Order

When two atomic orbitals combine, the result leads to produce two MOs, one bonding (lower energy) and the other antibonding (higher energy). The extent of bond formed between the two nuclei is measured qualitatively by bond order. Bond order is expressed as :

Bond order = (number of electrons present in the bonding orbital number of electrons present in the antibonding orbital) $\times \frac{1}{2}$.

Thus for hydrogen molecule Bond order = $\frac{2-0}{2} = 1$.

For He_2 molecule, Bond order = $\frac{2-2}{2} = 0$.

So He molecule does not exist.

2.13 Molecular orbitals of heteronuclear diatomic molecules

In developing a MO description for heteroneuclear diatomic molecules, we need to take into account the difference in electronegativities of the interacting atoms. Heteronuclear bonds will be formed between atoms with orbitals at different energies. When this occurs, the bonding electrons will be more stable in the presence of the nucleus of the atom having greater electronegativity, i.e. the atom having the lower atomic energy levels. The electron cloud will be distorted toward that nuclear and the bonding MO will resemble that AO (of the more electronegative atom) more than the AO on the less electronegative atom. The antibonding MO has more character of the AO of the less electronegative atom and the molecular system assumes some ionic character depending on the electronegativity difference of the combining atoms. As per LCAO, overlap of the orbitals of combining atoms are less effective (than homonuclear combination) as there is a difference in energies of the AOs. Heteronuclear diatomic molecules have no centre of inversion so that there are no 'g' or 'u' subscript in the MOs.

MO diagrams of some heteronuclear diatomic molecules are shown in Figure 8 (CO). Figure 9 (NO), Figure 10 (HF).

CO is isoelectronic with CN^- with 10 valence electrons (total 14 electrons). The bond order of CO and CN^- is 3.

NO molecule is odd electron molecule (11 valence electrons). There is one unpaired electron in π* orbital which is responsible for paramagnetism. Bond order of NO is 2.5. NO^+ will not have any unpaired electron in π* and the bond order will be 3 and therefore more stable than NO.

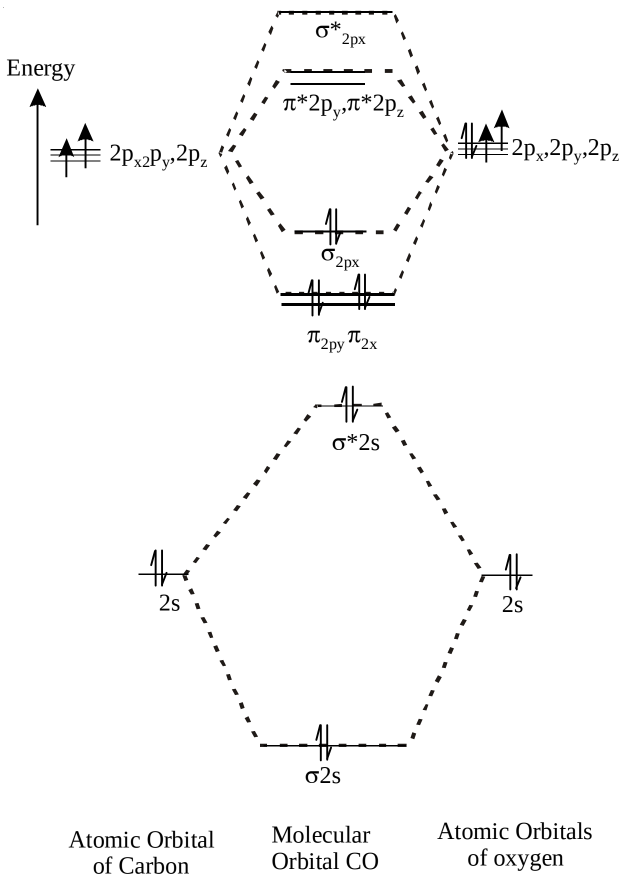


Fig. 8 MO diagram of CO

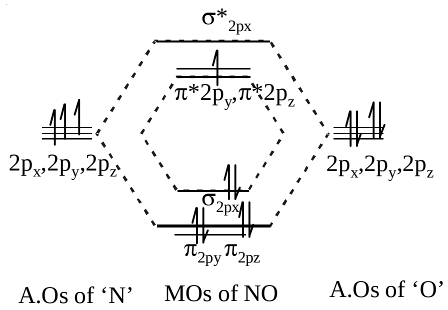


Fig. 9 MO energy level diagram of NO

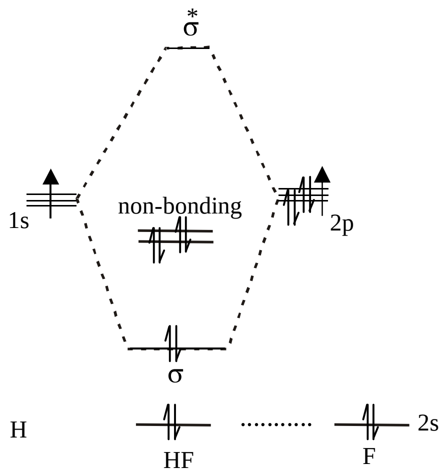


Fig. 10 MO energy level diagram of HF

Molecular orbitals of triatonic molecules or ions

H_2O molecule: The molecule is angular and central oxygen atom is sp^3 hybridised with total valence electrons = 2 + 6 = 8. The MO energy level is drawn with the consideration of overlap of four sp^3 hybrid orbitals of oxygen and two 1s orbitals of hydrogen (Figure 11). Two $\sigma^{nb}_{sp^3}$ MOs are occupied by lone pairs and the two $\sigma^{*}_{sp^3}$ antibonding orbitals remain unoccupied.

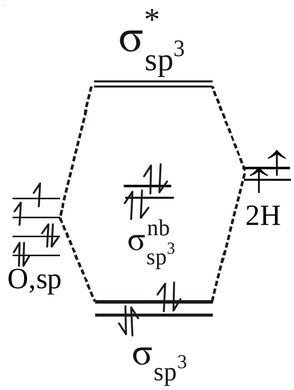


Fig. 11 MO energy level diagram of H_2O

BeH_2 : BeH_2 molecule is linear. The MOs for this molecule are constructed from 1s orbitals of H atoms (labelled H and H′) and 2s and one of the 2p orbitals of Be (the one directed along the H—Be—H bond axis). The remaining two 2p orbitals of Be cannot enter into the bonding because they are perpendicular to the molecular axis and have zero net overlap with H orbitals.

Four AOs enter into bonding, so four MOs will be formed. The bonding MOs are formed by linear combination of the atomic orbitals to give maximum overlap. Prior to formation of MOs, we can consider that the orbitals of two H-atoms combine into group orbitals. The group orbitals are formed by simply taking linear combinations of 1s orbitals of H and H′. The group orbitals correspond to $\psi_H + \psi_{H'}$ and $\psi_H - \psi_{H'}$. The first one is appropriate to overlap with Be 2s orbital, which is everywhere positive. The second one will form a bonding MO by overlapping with 2p orbital of Be which has one positive and one negative lobe. The antibonding orbitals will be formed by opposite combinations.

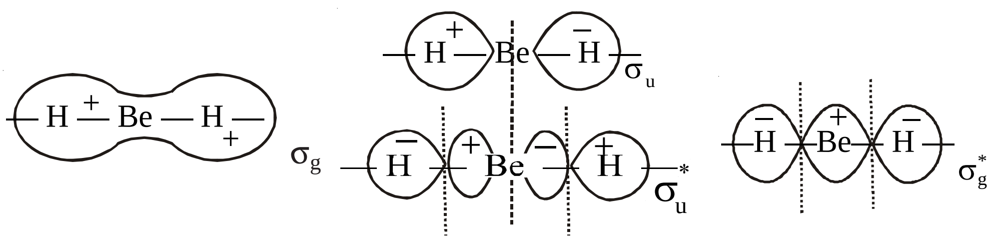


Fig. 12 Bonding and Antibonding MOs in BeH_2 molecule

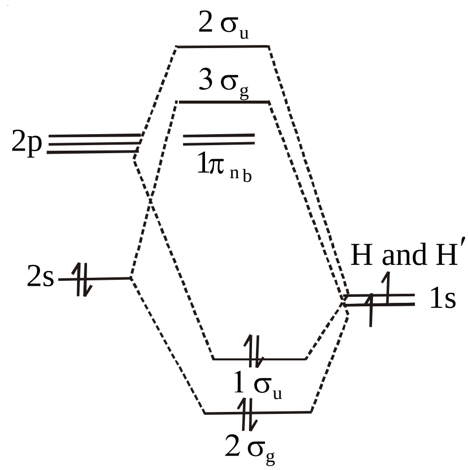


Fig. 13 MO energy levels in BeH_2 molecule

Figure 13 shows both the bonding MOs are delocalised over all three atoms. This is a general result of the MO treatment of polyatomic molecules. The lowest energy orbital, $1\sigma_g$ is not shown in the figure. It would be formed from the 1s orbital on Be, which interacts very little with H orbitals because of large energy difference. This MO is therefore non-bonding and essestially indistinguishable from Be 1s orbital.

2.14 Electron sea model and Band theory

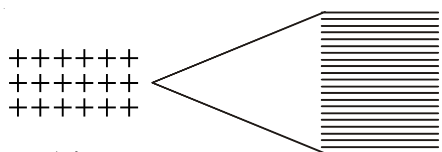
Generally metals have very distinctive properties. Specially, they are good electrical and thermal conductors, are very opaque, have high reflecting power i.e. lustrous, generally hard with high density at the same time ductile and malleable, have high melting and boiling points, have properties of alloy formation (i.e. formation of solid solution), photoelectric emission, thermoionic emission, electropositivity etc. All such properties cannot be explained by normal ionic and covalent bond models. A few theories have been proposed to explain the above properties of the metals.

1. Electron sea model (Also known as Drude-Lorentz theory). Generally metals are high density solid crystals. So the atoms are very closely packed and the outer most orbitals containing the valence electrons are not bound to any particular nucleus. The positive cores of the metal atoms constitute a joint lattice, the valence electrons occupy a combined molecular orbital space above the metal ion core to form a sea of electrons and weakly held to the Kernal or core in metals. Thus the free movement of electrons within the metal from one Kernal to other is explained. They are also called electron gas. As the electrons are free from influence of parent metal atom, they conduct electricity easily and

can be easily excited by visible light to give the lustrous nature. The melting point and boiling point of metals may be explained on the basis of cohesive force operated between two adjacent layers of metal lattice. In case of Na, one valence electron per atom contribute to the sea of electrons while Mg and Al contribute two and three valence electrons respectively per atom to the sea of electrons. Therefore the cohesive force between two adjacent layers of the metals is in the order Na < Mg < Al and so melting point and boiling point will be of the order Al > Mg > Na. The order of malleability and ductility is opposite to that of cahesive force, i.e. more the cohesive force, less will be the malleability and ductility. Among the above three metals, Al will have the least malleability and ductility while Na will have the highest and the order will be Na > Mg > Al.

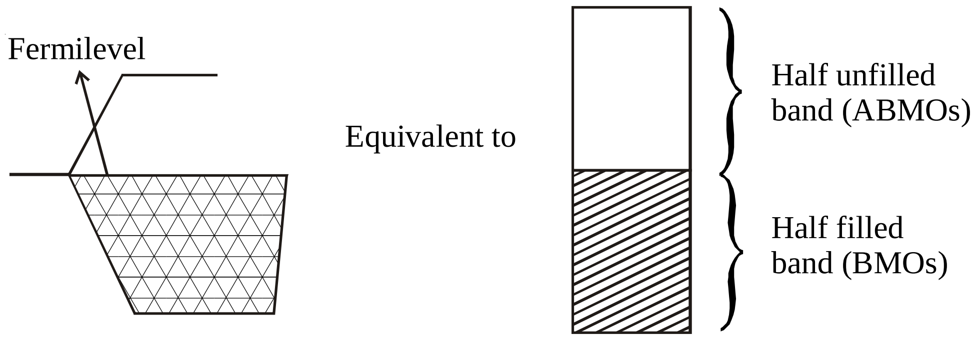
This model cannot explain the decrease in conductivity with rise in temperature and non-conductance of some metals in the solid state.

2. Band theory : Band theory can satisfactorily explain many properties of metals. This is an extersion of the MO theory for a large number of atoms. For homo nuclear diatomic molecule, two atomic orbitals combine to produce two new sets of orbitals between the two nuclei. This may be extended to a large number of orbitals. If ‘n’ number of metal atoms, each containing one outermost orbital to combine with other one, there will be produced ‘n’ number of MO’s. Those large number of MO energy levels will be spaced closely one upon another to form an energy band occupied by the valence electrons. A metal thus consists of energy bands formed by mixing the individual atomic orbitals.



‘n’ a.o s ‘n’ mos

For example the valence electron of sodium atom remains in 3s orbital. When two sodium atoms combine to form MO, two set of new orbital is formed just like hydrogen atoms. For total ‘n’ number of atomic orbitals, ‘n’ number of molecular orbitals will be formed half of which will be bonding and other half antibonding. If Avogadro number of Na atoms is present in the metal lattice (one mole) then Avogadro number (N) MOs will be formed. The 3s AO's of Na atoms have one electron each and so 'N' electrons will fill up $^N/_2$ MOs (2 electrons per MO) i.e. the bonding MOs, and $^N/_2$ MOs will remain empty.



Na metal therefore will be a conductor of electricity since the lower half filled band transfers electrons to the upper unoccupied half filled band easily. For alkaline earth metals such as Mg with $3s^2$ valence electron configuration, both the band (lower BMO and upper ABMO i.e. the 3s band) will be completely occupied and there is no scope for transfer of electrons from lower to upper band. But Mg is a metal and a good conductor of electricity at room temperature. This is due to the fact that the vacant 3p band overlap with 3s band to form an overlap zone and electrons can move easily from 3s to 3p band.

For Na metal, as stated above, lower half of 3s band is filled and the upper half empty. This statement is true at absolute zero (0K). At all real temperatures the Boltzmaun distribution together with closely spaced energy levels will ensure that the sharp cut-off shown in the figure is somewhat fuzzy. The top of the filled energy levels is termed the Fermi level.

As already stated, electrons can also occupy the Mo's formed by the p orbitals. In the case of Be (like Mg discussed earlier) each atom contain two electron in the valence shell. The 2s band will be complete and it will merge with the empty 2p band. Electrons now more to the vacant band on thermal or electrical excitation.

The band theory of solids:

The band theory may be extended to other non metallic sodids. Conduction of electricity are attributed to readily available electrons in their structure. In solid Neon [Ne(c)] atoms are held by weak van der waals force. There is a top level of filled 2p band, a narrow empty band of 3s. Since the bottom 2p band and top 3s bands are widely separated in the case of Neon, the excitition of electrons from 2p to 3s requirs high energy. So Ne(s) is expected to be an insulator. Similarly NaCl crystal will be an insulalor at ordinary temperature. Molecular crystals will behave in similar manner. Since weak van der waal force within the molecules give rise to narrow band widely separated from one another.

2.15 Classification of Inorganic solids and their conduction properties according to Band theory

The difference in energy ΔE between the highest occupied band, i.e. valence band, and lowest vacant band (the conduction band) in a solid (Figure 14) may be determined from the lowest frequency of absorption of uv or visible light by the solid. The elements of carbon family show an interesting trend ΔE.

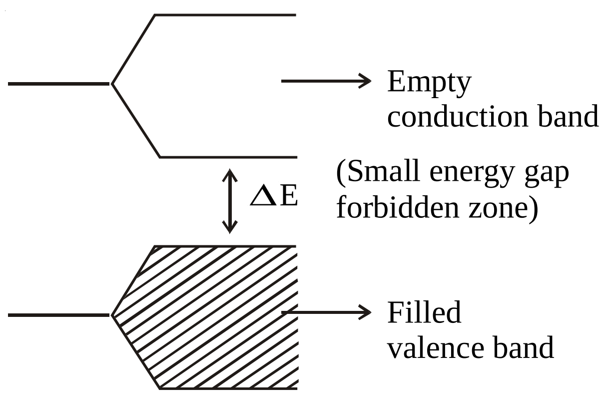


Figure 14. Energy band diagram of intrinsic semiconductor

ΔE (ev)	C(diamond)	C60	Si	ge	Sn(grey)	Pb
	6	1.7	1.2	0.7	0.08	0.0

Lead and tin (Sn) are typical elements whose electrical conductivity decreases with temperature. The band gaps of Si and Ge are small and can be overcome by thermally excited electrons. As T increases more electrons are excited to cross the gap. Therefore they show increase in electrical conductivity with increase in temperature. They are termed as semiconductors. The behaviour of these elements differ from others whose electrical conductivity decrease with temperature.

In intrinsic semiconductors the energy gap between a filled band and the next empty band is very small. The electrons cannot jump accross this gap, so the substance behaves like an insulator at absolute zero (0K). As temperature is raised the thermal energy gained by the electrons becomes sufficient to promote them to the next empty band, so conduction can occur. Pure germanium and grey tin are intrinsic semiconductors.

Semiconductor behaviour is seen in certain substances by deliberate addition of impurities. Such semiconductors are called **extringic semiconductors**. They are of two types:

1. n-type semiconductors : When arsenic or antimony (with 5 valence electrons) is added (diped) to germinium (4 valence electrons) produces a n-type semiconductor. The deliberately added impurities place a filled energy band just below the empty band of the metal (Ge for example). Electrons from the inpurities can be easily excited to the empty metal band. Here the conductivity results from the flow of electrons) and hence it is called a negative or n-type semiconductor (Figure 15).

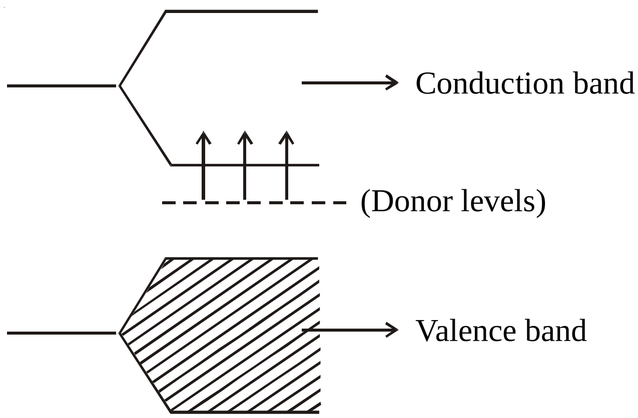


Figure 15. Conduction byelectrons in a donor or n-type semiconductor.

2. p-type semiconductors : When Germanium is doped with galium or indium (with 3 valence electrons), they place an empty band just above the filled metal band. Passage of electrons from germanium to these empty bands results in a number of vacant sites of the electrons on germinium which becomes positively charged. The vacant sites are called 'positive holes'. Adjacent electrons move to fill these positive holes, thus more positive holes are formed behind them. These seem to be that there is a migration of positive holes. Thus a positive or p-type semiconductor results (Figure 16).

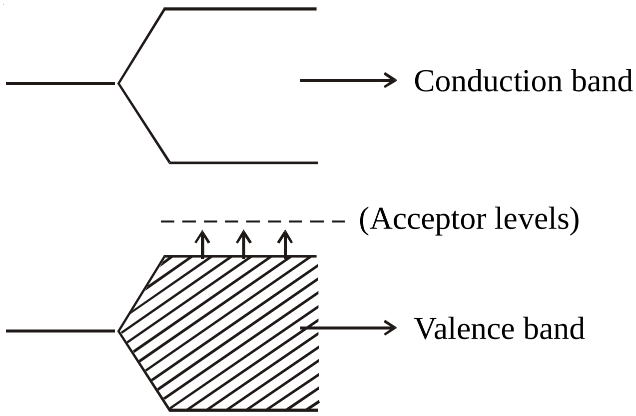


Figure 16. Conduction by holes in an acceptor or p-type semiconductor

Combination of n-type and p-type semiconductors produces an n-p junction. Electrons can flow from n to p, and holes from p to n and the current passes more easily in one direction than the other. It can act as a diode. Two n-type silicon separated by a weak p-type silicon produces a n-p-n junction or a transistor.

2.16 Hydrogen bonding

Hydrogen forms only monovalent compounds. When hydrogen is linked with highly electronegative elements like X=fluorine, oxygen, nitrogen another special situation arises. The bonded pair between H and X is shifted towards X and charge separation occurs. Thus hydrogen acquires a slight positive charge and the negative end of X gets associated with the δ+ hydrogen through a weak bond i.e. hydrogen froms a bridge between two highly electronegative atoms. This is called hydrogen bond, which is

$$\overset{\delta+}{H}\rightarrow\overset{\delta-}{X} \quad \rightarrow \quad \overset{\delta+}{H}\rightarrow\overset{\delta-}{X}\cdots\cdots\cdots\overset{\delta+}{H}-\overset{\delta-}{X}\cdots\cdots\overset{\delta+}{H}-\overset{\delta-}{X}$$

represented by broken line. It is defined as the attractive force which binds hydrogen of one molecule with electronegative atom of another molecule of the same substance.

The strength of hydrogen bond may vary widely. The enthalpy change is small for weak interaction (10-50 KJ mol^{-1}) and enthalpy change for strong interactions one 50-100 KJ mol^{-1}.

Effect of Hydrogen bonding

Molecules of water, ammonia, hydrogen fluoride etc. all are associated through hydrogen bonding. The effect is manifested in the boiling points of the molecules compared to the higher congeness of the group.

Boiting points (°C) of some Hydrogen bonded compounds

Bonded	H_2O	100	HF	19	C_2H_5OH	64.5
	H_2S	–60	HCl	–85	C_2H_5SH	5.8

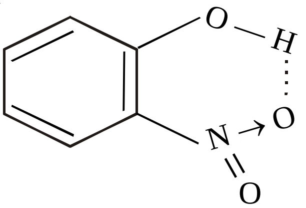
Hydrogen bonds may be of two types:

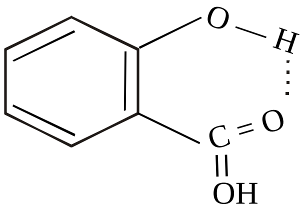
i) Intermolecular

ii) Intramolecular

i) Hydrogen bonds between several molecules are intermolecular hydrogen bond as in HF, H_2O, ammonia.

ii) Hydrogen bond formed in the same molecule is called intramolecular hydrogen bond, as in o-nitrophenol, salicylic acid etc.





In the intra molecular hydrogen bonded compounds, there is no association. Thus the boiling point of these compounds are lower than expected.

Hydrogen bond in Biological Systems:

Hydrogen bond plays an important role in the biological systems. Protein contains chains of amino a acid units arranged in a spiral form i.e. like stretched springs. The N—H group of each amino acid unit and the fourth C=O group following it along the chain forms N—H...O hydrogen bond. Thus the spiral structure becomes stable.

Nucleic acids also contain hydrogen bond. Hydrogen bonded water also plays a vital role in the life process.

2.17 Vander Waals forces

It is believed that there is no attractive force between the gas molecules. But the force though very weak in nature is responsible for liquifaction and solidification of gases. This force cannot be explained by the idea of ionic or co-valent bonds. The existance of a force in the non polar molecules like H_2, CH_4, He, Ne etc. was first recognized by van der Waals. So this type of inter molecular force is termed as van der waals forces. The van der Waals forces are best manifested in the molecular crystals of a variety of substances.

In graphite the hexagonal framework in one plane is held by covalent bonds but the layers of planes are held by weak van der Waals force. The layers easily slide over one another. Molybdenm sulphide MoS_2 form similar layer structures and used as a lubricant at high temperatures and called 'Moly slip'.

The strength of van der Waals force increases as the size of the unit increases. When other forces like Hydrogen bonding are absent this can be appreciated by the comparism of m.p. or b.p. such as $PbH_4 > SnH_4 > GeH_4 > SiH_4 > CH_4$ and b.p. of Ne 27.2K, He 4.2K etc.

Intermoleculer forces can originate from a variety of interactions involved between the molecules, such as :

1. Dipole-dipole interaction:

The potential energy of interaction between two dipoles having moments μ_A and μ_B in head to tail arrangement at a distance r is given by

$$E = -(\mu_A\mu_B/4\pi\varepsilon_0 r^3)$$

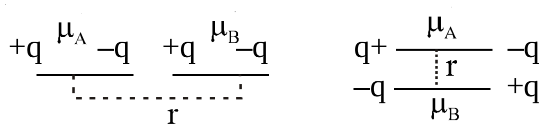
$$(4\pi\varepsilon_0 = \text{permitivity of the medium})$$

The result of higher power of r in the denominator is a sharper dependence on intermolecular distance and a smaller energy of interaction at ordinary temperature. The expression is comparable to KT at room temperature, and a realistic assessment of the interaction should allow for a Boltzmana distribution of orientations as the dipole molecules tumble. Using approcimation that E is less than KT, the average net energy of interaction is given by,

$$E = -\frac{2}{3}\frac{\left(\mu_A^2\mu_B^2\right)}{r^6(KT)} \times \frac{1}{\left(4\pi\varepsilon_0\right)^2}$$

[K = Boltzmann const.
T = Absolute temperature]

The dependence of this potential energy has now become $1/r^6$ which reduces the range of interaction sharply. E (dipole-dipole) is called Keesom energy which is inversely proportional to temperature. At higher temperature, the kinetic energy of the molecules increases and the molecules are randomly oriented, so that dipole-dipole interaction decreases.



Such interaction occour in liquid state HF, NF_3 etc.

2. Ion-dipole interactins:

The potential energy of interaction between an ion of charge number Z with a dipole of moment μ at is distance r :

$$E = -Z\mu e \;/\; 4\pi r^2 \varepsilon_0$$

Such interaction occurs in solovation and dissociatin of ionic compounds in polar solvents.

3. Monopole (Ion) — Induced dipole interaction:

Charged ions can polarize neutral molecules to change their electronic environment to induce a dipole moment. The energy of such interaction is

$$E = -(Ze)^2_\alpha / 2r^4 (4\pi \in_0)$$

The point charge has induced a dipole and the atom is said to be polarised. The induced dipole moment is proportional to the electrical field produced by the point charge and the proportionality constant is polarisibility $\mu_{induced} = \alpha.ri$

Z is the numerical charge of the ions, r the distance between them. α is the polarisiability of the molecule. A strong permanent dipole moment μ may also induce a dipole moment in nearby atoms or molecules and may act an ion.

$$E = \frac{-2\mu^2\alpha}{r^6(4\pi\varepsilon_0)}$$

This effect, like that between thermally averaged permanent dipoles, varies as $1/r^6$, and therefore, the range is extremely short, and energy of interaction is quite small. The force fall rapidly with the distance, involved in the dissolution of ionic or polar compounds in non polar solvents.

4. Instantacous dipole, induced dipole interaction, (or Induced dipole-induced dipole interaction)

Rapid continuous changes in the intensities of charge concentration in the electron atmosphere may give rise to instantaneous and fluctuating dipoles. These may induce further dipoles in adjacent molecules. The mean instantaneous dipole $\bar{\mu}$ and polarizability α gives the potential energy relation as : $E = \dfrac{2\bar{\mu}\alpha}{r^0 (4\pi \epsilon_0)}$

Or more conveniently as : $E = \dfrac{-3I\alpha^2}{4r^6(4\pi\varepsilon_0)}$ [I = Ionisation energy of the molecule]

The resulting weak short ranged force is called London dispersion force or dispersion force. Usually this force is related to molecular weight but polarizability plays an important role. This is only one of the forces considered that can produce a net attraction between two electrically neutral atoms or nonpolar molecules. It constitutes the entire binding energy in genuinely covalent molecular crystals such as those of the noble gases or elemental halogens. So such crystals should sublime or boil at temperatures at which KT is comparable to this energy. Ar boils at 87K, Kr at 121K, Xe at 165K, Fat 85K, Cl at 239K. The interaction is independent of temperature and operate at all temperatures in case of real gas molecules. These London forces are responsible for variation of boiling points of inert gases at stated above. It increases with increasing polarisibility of molecules or atoms. The polarisibily depends on molecular or atomic size which in term is related to molecular weight or atomic weight. Boiling point of hydrides of Group 14 are of the order $CH_4 < SiH_4 < GeH_4 < SnH_4$.

The intermolecular forces that are responsible for non-ideality in gases are limited to those that involve only dipoles and induced dipoles. There are only three of these, all relatively weak. The dipole-dipole interaction, dipole-induced dipole interaction and the London dispersion energy. All of these have $1/r^6$ dependence, so that they are lumped together as van der Waals forces.

2.18 Summary

1. Lewis Structure, presentation of electrons in a molecule as dot (.). Two dots form a bond. Octet rule is obeyed in the structure (2 for H & He).

2. Formal Charge, i.e. the hypothetical charge acquired by the atom assuming equal sharing of bonding electrons.

   Calculation of Formal Charge in molecules & ions.

3. Valence bond theory: Idea of bond formation, through spin pairing application of schrödinger wave equation.

4. Directional properties of covalent bond: Hybridisation and shapes of molecules, VSEPR Theory.

5. Concept of Equivalent and non equivatent hybrid orbitals.

6. Stereochemistry of non rigid molecules, Rotation along a bond.

   Berry pseudorotation in inorganic molecules.

7. Idea of Resonance and dipole moment of inorganic molecules.

8. VSEPR Theory and Bent's rules distribution of ligands along the axis.

9. **Molecular orbital theory :**

   Linear combination of atomic orbitals.

   Bond order.

   M.O. diagram of homo nuclear diatomic molecules.

   Hetero nuclear diatomic and some triatomic molecules.

   σ and Π orbitals, non bonding orbitals.

10. **Band theory:** Conduction band of aggregate of atomic orbitals in closely spaced orbitals.

    Electron sea model: All the valence electrons are present over the surface of the metal.

11. **Classification of inorganic solids:** Conductor, semiconductors and transistors.

12. **Hydrogen bonding:** The interaction of the type X—H·····Y where X and Y are highly electronegative atoms. H-bond is weaker than the covalent bond. Hydrogen bonding is extremely important for the physical properties and structural orientation of molecules.

13. **Van der Waals forces:** This type of interaction is observed in closed shell

molecules involved in weak interaction between ions or dipoles, London dispersion interaction etc.

2.19 Self Assessment Questions

Unit 2

Chemical Bonding II : Covalent Bond.

Sub Unit 1 and 2 (Lewis Structure, Formal charge.

Q1. a) What is the importance of Octet rule (doublet for H) in the formation of covalent compounds?

b) Write down the Lewis dot structures for the following compounds.

BF_4^-, H_2O, C_2H_4, NH_3, H_2SO_4, HN_3, HNO_2, H_3PO_3 and benzene.

c) There are many compounds which do not obey the octet rule: explain with examples what are the defects of Lewis dot structure?

Q2. Define formal charge.

State with example how the formal charge of an atom in a molecule can be calculated.

Q3. What is expanded octet.

Q4. Draw the Lewis dot structure of $IO_2F_2^-$ and calculate the formal charge on iodine atom.

Q5. Calculate the formal charge on constituent atoms in BF_3.

Sub Unit 3 : VBT

Q1 a) State the basic idea of valence bond theory. Explain with diagram, the theoretical energy curves for hydrogen molecule.

b) How does the idea of spin pairing appears in the valence bond approach to the H_2 molecule.

c) Explain in the light of valence bond theory, the localized bond formed between the two nuclei and that directional character of atomic orbitals gives rise to directional character of the bond.

Sub unit : 4 & 5 : Directional properties of covalent. & 6 Equivalent and Non-equivalent hybridization.

Q1. State VSEPR theory to predict the shapes of covalent molecules.

Q2. Explain why the repulsion of lonepair-lonepair is greater than that of lonepair-bondpair and bondpair-bondpair.

Q3. a) Predict the structure of ClF_3 according to VSEPR theory.

b) What are stereochemically non rigid molecules?

Q4. i) XeF_2 is linear—explain from the VSEPR theory.

ii) Describe the molecule geometry of XeO_3F_2 in light of VSEPR theory.

Q5 Explain :

a) In NH_3 HNH bond angle is 107.3°

In PH_3 HPH bond angle is 93.3°

b) In water ∠HOH = 104° & in H_2S ∠HSH = 92.2°.

Q6. Establish the idea of hybridization in light of VSEPR Theory.

What are equivalent and non-equivalent hybrid orbitals, cite examples.

Q7. Explain Berry psendo rotation with suitable example and mechanism.

Submit 7 : Resonance, Dipole moments

Q1. State the condition that the different resonating structures should obey.

Q2. i) Draw all thye canonical froms of O_3, N_3^-, NO_2^-, CO, $CO_3^=$ and state which one is of lowest every for each case.

ii) N_3^- is more resonance stabilized than HN_3 : Explain

Q3. Which of the following molecules are expected to have parmanent electrical dipole moment? SO_2, SF_2, SF_4, S_2Cl_2, C_2H_2, SiF_4, BCl_3, N_2F_4, PF_5, BrF_5, XeF_4, O_2 and O_3.

Q4. The dipole moment of water is 6.17×10^{-30} Cm. The HOH angle is 104° and O–H distance is 96 pm. Calculate the percent iomic character and bond moment of O – H bond.

Q5. The dipole moment of CH_3F and CHF_3 are comparable—Explain.

Q6. Dipole moment of CO molecule is less than expected from the electronegativity differnce—explain.

Sub unit 8 : (VSEPR Theory and Bent's rules)

Q1. In light of VSEPR Theory describe the equivalent and non-equivalent hybrid orbitals.

Q2. State Bent's rules and explain with examples.

Q3. The P.F bond lengths in PF_5 are as follows—

axial P — F = 157.7 pm.

equitorial P — F = 153.5 pm.

— Explain.

Q4. In CH_2F_2 the HCH angle is 111.9° where as FCF angle is 108.3°—Explain.

Q5. Draw the structures of the following molecules according to VSEPR Theory

SF_4, PCl_4^-, H_3O^+, IF_5, IF_7, ClF_3, IF_3.

Sub unit 9 : M.O. Theory

Q1. a) What are bonding, anti-bonding and non-bonding molecular orbitals?

b) Define bond order. Show that He_2 molecule does not exist.

c) State and explain with reasons the expected change in the bond orders and bond distances in the following isolectronic species.

$O_2 \rightarrow O_2^+$

$N_2^+ \rightarrow N_2$

d) Draw the MO energy level diagram for HF, CO, NO, NO^+ CN^-, H_2O and BeH_2.

e) Predict the magnetic properties (paramagnetic or, diamagnetic) of B_2 and C_2 molecules from M.O. energy level diagram.

f) Construct the MO energy level diagram for H_2O molecule and hence predict the nature of bonds formed.

Sub unit 10 and 11 : (Band Theory)

Q1. Write short accounts on Electron sea model and Band Theory for metals.

Q2. What is Fermi Level? What is n-p-n junction?

Q3. Define semiconductors. What is Doping? What are n-type and p-type semiconductors?

Q4. The solid alkali metals are slightly paramagnetic—explain in the light of band theory.

Q5. State and explain the beharrions of metals and semiconductors in respect of their conduction properties when temperature increases.

Sub unit 12 and 13 : (Hydrogen Bonding, Van der Waals forces)

Q1. Define hydrogen bonding.

Q2. State the effect of hydrogen bonding on the physical properties of compounds, (M.P., B.P., Vaporisation etc.)

Q3. What are inter molecular and intra molecular hydrogen bonding? Explain with examples.

Q4. State the effect of hydrogen bonding in the biological systems.

Q5. Define Van der Waals forces with examples.

Q6. What are—

a) Dipole-dipole interaction?

b) Ion-dipole interaction?

c) Ion-induced dipole interaction?

d) Instantaneons dipole-induced dipole interaction?

What is London force?

2.20 Further Reading

1. General and Inorganic Chemistry, Vol. I and Vol. II, R. P. Sarkar, Books and Allied (P) Ltd.
2. Chemistry of Elements, Greenwood and Earnshaw, Maxwell and MacMillan.
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4. Inorganic Chemistry, Principle of Structure and Reactivity, Huheey, Keiter and Keiter.
5. Inorganic Chemistry, Miessler an Tarr, Pearson Education.
6. Essential Trend in Inorganic Chemistry, D.M.P. Mingos, Oxford (Indian Ed.)
7. Fundamental Concepts of Inorganic Chemistry, A. K. Das, and M. Das, Volume 4, 1st Ed. 2016.
8. Importance of Anti Bonding Orbital, Jaffe and Orchin, Oxford and IBH Publishing Co.
9. Inorganic Chemistry, G. Wulfsberg, Viva
10. Concepts and Modals of Inorganic Chemistry, Douglas, McDaniel, Alexander. Wiley, Students Edition.

Unit 3 ❑ Coodination Chemistry-1

3.0 Objectives

After reading this unit you can be able to know

* definition of double salt and complex salt.
* Details of Werner's theory
* EAN-rule
* Definition of ligands and their classification
* IUPAC nomenclature of coordination compounds
* Concept on streochemistry and isomerism of complexes.

3.1 Introduction

Coordination chemistry is the study of compounds that have a central atom generally metallic surrounded by molecules or anions known as ligands. The ligands are attached to the central atom by dative bonds. Known as coordinate bonds, in which both the electrons in the bond are supplied by the same atom on the ligand.

In Coordination chemistry, a ligand is an ion a molecule that binds to a central atom to for a coordinaton complex. The bonding with the metal generally involves formal donation of one or more of the ligands electron pairs often through lewis bases.

3.2 Double salts complex salts

Double salts: They usually contain two simple salts in equimolar proportions. They exist in the solid state. In aqueous solutions, they dissociate completely into the corresponding ions of the individual components and give the test of all their constituent ions. They don't contain any coordinate bonds since they are ionic in nature. They exhibit properties similar to that of the consisting ions.The metal ions present in double salts show their normal valency.

Example: KCl $MgCl_2 \cdot 6H_2O$, $K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ etc.

Complex salts: The properties of different salts present in a complex salt may or may not be same. The complex salts can exist both in solid state as well as in aqueous solution. Complexes may or may not be ionic but the complex part will always contain coordinate bonds. They exhibit two types of valencies - primary and secondary. A complex compound contains a simple cation and a complex anion or a complex cation and a simple anion or a complex cation and complex anion. The term complex compound is used synonymously with the term coordination compound.

Example: $K_4[Fe(CN)_6]$, $[Co(H_2O)_6]CI_3$, $[Co(NH_3)_6]$ $[Cr(C_2O_4)_3]$ etc.

3.3 Werner's theory

Alfred Werner in 1823, formulated his theory to describe the.structure and formation of complex compounds or coordination compounds. In a series of compounds of cobalt(lll) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess silver nitrate solution in cold but some remained in solution.

1 mol $CoCl_3 \cdot 6NH_3$ (Yellow) $\rightarrow$ 3 mol AgCl

1 mol $CoCl_3 \cdot 5NH_3$ (Purple) $\rightarrow$ 2 mol AgCl

1 mol $CoCl_3 \cdot 4NH_3$ (Green) $\rightarrow$ I mol AgCl

I mol $CoCl_3 \cdot 4NH_3$ (Violet) $\rightarrow$ 1 mol AgCl

On the basis of the observations Werner postulated the following points.

Postulates of Werner's Theory:

1. The central metal ions or the metal atoms in coordination compounds show two types of valency. They are the primary and secondary valency.
2. The primary valency relates to the oxidation state and the secondary valency

relates to the coordination number. Primary valency is also called principal, ionisable or ionic valency, and secondary valency is non-ionic or non-ionisable.

3. The number of secondary valences is fixed for every metal atom or ion. It means that the coordination number is fixed.

4. The metal atom or ion works towards satisfying both its primary and secondarv valencies A negative ion satisfies the primary valency. On the other hand, negative ions or neutral molecules satisfy secondary valencies. The ions or molecules which satisfy secondary valency or coordination number are directly attached to metal atom or ion. An anion can show a dual behaviour i.e. it may satisfy both primary and secondary valencies.

5. The secondary valencies point towards a fixed position in space. This is the reason behind the definite geometry of the coordinate compounds. For example, let us consider the case of a metal ion having six secondary valencies. They arrange octahedrally around the central metal ion or atom. If the metal ion has four secondary valencies, they arrange in either tetrahedral or square planar arrangement around the central metal ion or atom. Therefore, we see that the secondary valency determines the stereochemistry of the complex ion. On the other hand. the primary valency is non-directional.

Examples Based on Postulates of Werner's Theory

Werner's theory is responsible for the formation of' structures of various cobalt amines. We will look at its explanation now. Cobalt has a primary valency (oxidation state) of three and exhibits secondary valency (coordination number) of 6. Werner represented the secondary valencies by thick lines (solid lines) and the primary valency by dashed lines (broken lines).

1) $CoCl_3{\cdot}6NH_3$ Complex: In this compound, the coordination number of cobalt (III) is 6 and NH_3 molecules satisfy all the 6 secondary valencies by binding to the metal centre by coordinate covalent bonds to form the inner coordination sphere Chloride ions satisfy the 3 primary valencies. These are non-directional in character. These chloride ions instantaneously precipitate on the addition of silver nitrate. The total number of ions, in this case, is 4, three chloride ions and one complex ion. The coordination sphere is shown within square bracket [ ] and moietics bound by primary valence outside the bracket in formulation of the compound, which is called outer coordination sphere.

2) $CoCl_3{\cdot}5NH_3$ complex: In this compound- cobalt has coordination number of 6. However, we" see that the number of NH_3 molecules decreases to 5. The chloride ion occupies the remaining one position of coordination. This chloride ion exhibits the dual behaviour as it satisfies the primary as well as the secondary valency. Werner showed its attachment with the central metal ion by a combined dashed—solid line.

3) $CoCl_3·4NH_3$ complex: In this compound, two chloride ions exhibit the dual behaviour of satisfying both primary and secondary valencies. This compound gives a precipitate with silver nitrate corresponding to only one chloride ion and the total number of ions in this case, is 2. Hence, we can formulate it as $[CoCl_2(NH_3)_4]Cl$. (See Figure 1) Note : The coordination number of Co (III) (i.e. secondary valency) is always 6.

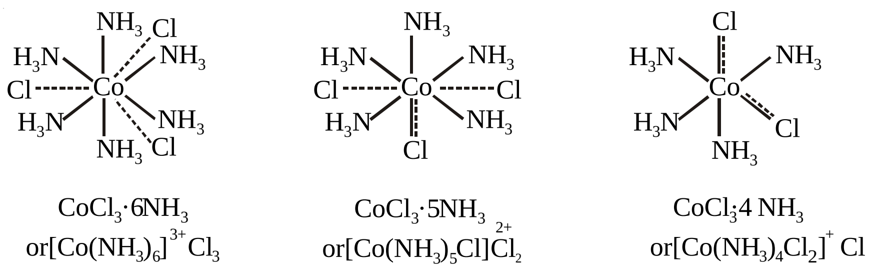


Fig. 1 Designations and formulations of Co (III) ammires on the basis of Werner's theory.

3.4 EAN Rule

With the advent of electronic theory of valency, it was considered necessary to make some modifications of Werner's theory. Sidgwick adopted the Lewis concept of two-electron covalent bond between two atoms in a molecule and introduced the new concept of coordinate bond (also called dative bond).

The effective atomic number (EAN) of an atom is the number of protons that an electron in the element effectively 'sees' due to screening by inner-shell electrons. It is a measure of the electrostatic interaction between the negatively charged electrons and positively charged protons in the atom. One can view the electrons in an atom as being 'stacked' by energy outside the nucleus with the lowest energy electrons (such as the I s and 2s electrons) occupying the space closest to the nucleus. and electrons of higher energy are located further from the nucleus. The binding energy of an electron, or the energy needed to remove the electron from the atom, is a function of the electrostatic interaction between the negatively charged electrons and the positively charged nucleus. In iron, atomic number 26, for instance, the nucleus contains 26 protons. The electrons that are closest to the nucleus will 'see' nearlv all of them. However, electrons further away are screened from the nucleus by other electrons in between and, feel less electrostatic interaction as a result. The 1s electron of iron (the closest one to the nucleus).sees an effective atomic number (number of protons) of 25. The reason why it is not 26 is because some of the electrons in the atom end up repelling the others, giving a net lower electrostatic interaction with the nucleus. One way of envisioning this effect is to imagine the Is electron sitting on one side of the 26 protons in the nucleus, with another electron sitting on the other side; each electron will feci less than the attractive force of 26 protons because the other electron contributes a repelling force. The 4s electrons in iron, which are furthest from the nucleus, feel an effective atomic number of only 5.43 because of the 25 electrons in between it and the nucleus screening the charge.

According to Sidguick's concept, the ligands attached with the central metal ion or atom have atoms which have at least one unshared electron pair and donate this pair to the central metal for attachment. The bond thus established between the ligand and the metal is a coordinate or dative bond. This bond is not different from a covalent bond except that the ligand (donor) has donated the electron pair to the metal ion or atom (acceptor) and represented as M ← L. Thus the structure of $[Co(NH_3)_6]^{3+}$ can be shown as Figure 2.

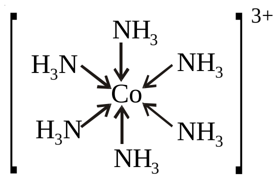


Fig. 2 (NH_3 molecules are the ligands and Co^{+3} the metal ion)

[Presently the bonds within the coordination sphere is not designated by an arrow to denote coordinate linkage, but by simple solid lines as given for covalent bonds.]

Effective atomic number (EAN) is number that represents the total number of electrons surrounding the nucleus of a metal atom or ion in a metal complex. It is composed of the metal atom's (or ion's) electrons and the bonding electrons from the surrounding electron-donating atoms and molecules. Thus the effective atomic number of the cobalt ion in the complex $[Co(NH_3)_6]^{3+}$ is 36, the sum ol the number of electrons in the trivalent cobalt ion (24) and the number of bonding electrons from six surrounding ammonia molecules, each of which contributes an electron pair (2×6=12). EAN 36 of Co (III) is equal to the atomic number of Kr.

Generally EAN of central metal will be equal to the number of electrons in the nearest noble gas. If the EAN of the central metal is equal to the number of electrons in the nearest noble gas then the complex possess greater stability.

EAN = [(atomic number of central metal atom) - (the oxidation state of the metal) + (the number of electrons gained by the metal from the ligands through co-ordination)] or,

EAN = [Z metal - (oxidation state of the metal) + 2(coordination number of the metal)].

Example:

1. $[Co(NH_3)_6]^{3+}$ → EAN = [27 – 3 + 2(6)] = 36
2. $[MnCl_4]^{2-}$ → EAN = [25 – 3 + 8] = 31
3. $[Fe(CN)_6]^{4-}$ → EAN = [26 – 2 + 12] = 36
4. $[CoF_6]^{3-}$ → EAN = [27 – 3 + 12] = 36
5. $[Cr(H_2O)_6]^{3+}$ → EAN = [24 – 3 + 12] = 33
6. $Ni(CO)_4$ → EAN = [28 – 0 + 8] = 36
7. $[Cu(NH_3)_4]^{2+}$ → EAN = [29 – 2 + 8] = 35
8. $[Pt(NH_3)_4]^{2+}$ → EAN = [78 – 2 + 8] = 84
9. $[PtCl_4]^{2-}$ → EAN = [78 – 2 + 8] = 84
10. $[PtCl_6]^{2-}$ → EAN = [78 – 4 + 12] = 86

Exceptions:

As seen from the examples not all complexes follow EAN rule. Complexes of Ni(II), Co(II), Ag(I) etc., which have more than one possible coordination number, depending on the nature of the ligand, generally do not follow the rule.

3.5 Classification of ligands and their binding modes:

Coordination compounds generally consist of a central metal atom or ion bonded to a fixed number of ions or molecules called ligands. The term 'dentate' means 'toothed', i.e. the number of position taken up by the ligand around the central metal atom or ion is its denticity.

Ligands : These are the ions or molecules bound to the central atom/ion in the coordination entity (sphere). They may be simple ions such as Cl^-, small molecules such as H_2O or NH_3, larger molecules such as $H_2NCH_2CH_2NH_2$ or $N(CH_2CH_2NH_2)$; or even macromolecules, such as proteins.

Unidentate or mono dertate ligands : When a ligand is bound to a metal ion or atom through a single donor atom, as with Cl^-, H_2O or NH_3, the ligand is said to be unidentate. They coordinate to the central metal atom or ion at one site only.

Bidentate ligands : When a ligand can bind through two donor atoms as in $H_2NCH_2CH_2NH_2$ (ethane- 1,2-diamine) or $C_2O_4^{2-}$ (oxalate), the ligands are said to be bidentate ligands. They take up two sites around the central metal.

Polydentate or multidentate ligands : When several donor atoms are present in a single ligand as in $N(CH_2CH_2NH_2)_3$, the ligand is said to be polydentate. Ethylenediaminetetraacetate ion ($EDTA^{4-}$) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

Chelating ligands : When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion or atom simultaneously and thus produce one or more rings around the central atom or ion, are called chelate (pronounced Kelate)or chelating ligands (from Greek 'crab's claw'). The number of such ligating groups (donor atoms) is called the denticity of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands. Porphyrins are complexes containing a form of the porphin molecule shown in Figure 3. Important biomolecules like heme and chlorophyll are porphyrins. Chelating ligands form more stable complexes than ordinary ligands. This is also called the chelate effect. The stability of chelate depends upon the number of atoms in the ring.

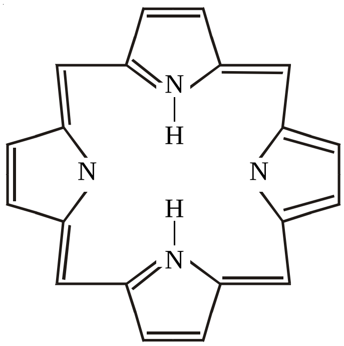


Figure 3

Generally, chelating ligands which do not contain double bonds form stable complexes with five membered rings. On the other hand, the chelating ligands which contain double bonds form stable complexes with six membered rings. Chelating ligands with smaller groups form stable complexes, than with larger and bulky groups. This is because of steric reasons.

Ambidentate ligands : Ligands which can ligate through two or more different atoms, but in forming complexes only one donor atom is utilised for attachment at a given time are called ambidentate ligands. Examples of such ligands are the NO^{2-} and SCN^- ions. NO^{2-} ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion. Similarly. SCN^- ion can coordinate through the sulphur or nitrogen atom. Other examples are CN^-, $S_2O_3^{2-}$, R_2SO, $SeCN^-$ etc.

Coordination number : The coordination number of a metal ion or atom in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded by σ bonds. For example, in the complex ions, $[PtCI_6]^{2-}$ and $[Ni(H_2O)_4]^{2+}$, the coordination number of Pt (IV) and Ni (II) are 6 and 4 respectively.

3.6 IUPAC nomenclature of coordination compounds:

Rules for IUPAC nomenclature of coordination compounds:

In a coordination entity

1. The cation is named first in both positively and negatively charged coordination entities.
2. The ligands are named in an alphabetical order before the name of the central atom/ion. The prefixes di, tri, etc. are not to be considered while determining this alphabetical order.
3. Names of the anionic ligands end in –o, those of neutral ligands are the same except H_2O which is named aqua, NH_3 which is named ainmine, CO which is named carbonyl and NO which is named nitrosyl. These are placed within brackets ( ). Positively charged ligands have suffix –ium, e.g. $NH_2NH_3^+$ is hydrazinium and NO^+ is nitrosilium.
4. Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity.
5. When the names of the ligands include a numerical prefix, then the terms, bis, tris, tetrakis are used, the ligand to which they refer being placed in parenthesis.
6. Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis ( ).
7. If the complex ion is a cation, the metal is named same as the element.
8. If the complex ion is an anion, the name of the metal ends with the suffix. —ate.
9. For some metals, the Latin names are used in the complex anions, e.g.. ferrate for Fe.
10. The neutral complex molecule is named similar to that of the complex cation.
11. Complexes with two or more metal atoms/ions in the coordination sphere are called polynuclear complexes. In these complexes, the bridging group is indicated by separating it from the rest of the complex by hyphens and adding prefix μ before its name. μ should be repeated before the name of each bridging group. Two or more bridging groups of the same kind are indicated by di–μ–, tri-μ-, etc.

12. A gap should be left between naming of moieties outside and inside the coordination sphere e.g. $K_2[CoCl_4]$ is potassium tetrachlorocobaltate (II) or $[Co(NH_3)_6]$ d_3 is hexaamminecobalt (III) chloride. No gap is given in naming the moieties within the coordination sphere.

Names of Some Common Ligands

Anionic Ligands	Names
Br^-	bromo
F^-	fluoro
O^{2-}	oxo
OH^-	hydroxo
CN^-	cyano
$C_2O_4^{2-}$	oxalato
CO_3^{2-}	carbonato
CH_3COO^-	acetato

Neutral Ligands	Names
NH_3	ammine
H_2O	aqua
NO	Nitrosvl
CO	Carbonyl
O_2	dioxygen
N_2	dinitrogen
C_5H_5N	pyridine
$H_2NCH_2CH_2NH_2$	ethylenediamine.

Name of Metals in Anionic Complexes

Name of Metal	Name in an Anionic Complex
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate

Name of Metal	Name in an Anionic Complex
Silver	Argenate
Gold	Aurate
Tin	Stannate

Examples:

SI. No.	Coordination Entity	IUPAC Name
I.	$[Cr(NH_3)_3(H_2O)_3]Cl_3$	triamminetriaquachromium(III) chloride
2.	$[Pt(NH_3)_5Cl]Br_3$	pentaamminechloroplatinum(V) bromide
3.	$[Pt(H_2NCH_2CH_2NH_2)_2Cl_2]Cl_2$	dichlorobis(ethylenediamine)platinum(IV) chloride
4.	$[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$	tris(ethylenediamine)cobalt(III) sulfate
5.	$K_4[Fe(CN)_6]$	potassium hexacyanoferrate(II)

6.	$Na_2[NiCl_4]$	sodium tetrachloronickelate(II)
7.	$Pt(NH_3)_2Cl_4$	diamminetetrachloroplatinum(IV)
8.	$Fe(CO)_5$	pentacarbonyliron(O)
9.	$(NH_4)_2[Ni(C_2O_4)_2(H_2O)_2]$	ammonium diaquabis (oxalato) nickelate(II)
10.	$[Ag(NH_3)_2][Ag(CN)_2]$	diamminesilver(I) dicyanoargentate(I)
11.	$[Fe(NH_3)_6](NO_3)_3$	hexaammineiron(III) nitrate
12.	$(NH_4)_2[CuCl_4]$	ammonium tetrachlorocuprate(II)
13.	$Na_3[FeCl(CN)_5]$	sodium monochloropentacyanoferrate(III)
14.	$K_3[CoF_6]$	potassium hexafluorocobaltate(III)
15.	$[CoBr(NH_3)_5]SO_4$	pentaamminebromocobalt (III) sulfate
16.	$[Fe(NH_3)_6][Cr(CN)_6]$	hexaammineiron(III) hexacyanochromate (III)
17.	$[Co(SO_4)(NH_3)_5]_4$	pentaamminesulfatocobalt(III) ion
18.	$[Fe(OH)(H_2O)_5]^{2+}$	pentaaquahydroxoironf III) ion
19.	$[(NH_3)_5\,Cr{-}OH{-}Cr(NH_3)_5]Cl_5$	µ-hydroxo-bis {pentaamminechromium (III) chloride or, pentamminechromium (III)-µ-hydroxo-chromium (III) chloride.
20.	$[(NH_3)_4\,Co(NH_2)(OH)Co\,(NH_3)_4]Cl_4$ (Co–Co bridged by NH_2 and OH)	µ-amido-µ-hydroxo-octaammire dicobalt (iii) chloride.

3.7 Overall and stepwise stability constants:

The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The magnitude of the (stability or formation) equilibrium constant for the association, quantitatively expresses the stability . Thus, if we have a reaction of the type:

$$M + 4L \rightleftharpoons ML_4 \text{ (M = mental ion/atom, L = monodentate ligand,}$$

$$\text{4 = coordination number)}$$

then, the larger the stability constant, the higher the proportion of ML_4that exists in solution. Free metal ions rarely exist in the solution so that M will usually be surrounded by solvent molecules which will compete with the ligand molecules, L, and be successively replaced by them. For simplicity, we generally ignore these solvent molecules and charge of the complexes and write four stability constants as follows:

$$M + L \rightleftharpoons ML; K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2; K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \rightleftharpoons ML_3; K_3 = \frac{[ML_3]}{[ML_2][L]}$$

$$ML_3 + L \rightleftharpoons ML_4; K_4 = \frac{[ML_4]}{[ML_3][L]}$$

where K_1, K_2, etc., are referred to as stepwise stability constants. [ ] represents concentration of the species.

Alternatively, we can express the stability constants as :

$$M + L \rightleftharpoons ML \quad \beta_1 = \frac{[ML]}{[M][L]}$$

$$M + 2L \rightleftharpoons ML_2 \quad \beta_2 = \frac{[ML_2]}{[M][L]^2}$$

$$M + 3L \rightleftharpoons ML_3 \quad \beta_3 = \frac{[ML_3]}{[M][L]^3}$$

$$M + 4L \rightleftharpoons ML_4 \quad \beta_4 = \frac{[ML_4]}{[M][L]^4}$$

where β_1, β_2 etc. are called overall stability constants.

The stepwise and overall stability constant are therefore related as follows:

$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$ or more generally, $\beta_n = K_1 \times K_2 \times K_3 \times K_4 ......K_n$

If we take as an example the steps involved in the formation of the cuprammonium ion. we have the following:

$$Cu^{2+} + NH_3 \rightleftharpoons Cu(NH_3)^{2+} ; K_1 = \frac{[Cu(NH_3)]^{2+}}{[Cu^{2+}][NH_3]}$$

$$Cu(NH_3)^{2+} + NH_3 \; f \; [Cu(NH_3)_2{}^{2+}] \; ; \; K_2 = \frac{[Cu(NH_3)_2]^{2+}}{[Cu(NH_3)]^{2+}[NH_3]}$$

$$[Cu(NH_3)_2]^{2+} + NH_3 \; f \; [Cu(NH_3)_3]^{2+} \; ; \; K_3 = \frac{[Cu(NH_3)_3]^{2+}}{[Cu(NH_3)_2]^{2+}[NH_3]}$$

$$[Cu(NH_3)_3]^{2+} + NH_3 \; f \; [Cu(NH_3)_4]^{2+} \; ; \; K_4 = \frac{[Cu(NH_3)_4]^{2+}}{[Cu(NH_3)_3]^{2+}[NH_3]}$$

where K_1, K_2 ...are the stepwise stability constants the overall stability constant is given by

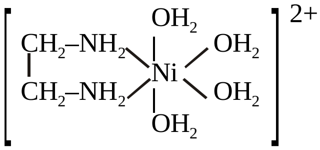
$$Cu^{2+} + 4NH_3 \; f \; [Cu(NH_3)_4)^{2+} \; ; \; \beta_4 = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}$$

3.8 Chelates:

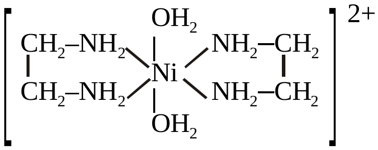
When bidentate or polydentate (multidentate) ligands form complexes through chelation, the stability constant increases. This is why, even for similar binding sites, chelating ligands form more stable complexes than non-chelating ligands (i.e. monodentate ligands).

Many essential biological chemicals are chelates. Chelates play important roles in oxsgen transport and in photosynthesis. Furthermore, many biological catalysts (enzymes) are chelates. In addition to their significance in living organisms, chelates are also economically important, both as products in themselves and as agents in the production of other chemicals. A chelate is a chemical compound composed of a metal ion or atom and a chelating agent. A chelating agent is a substance whose molecules can form several bonds to a single metal ion. In other words, a chelating agent is a multidentate ligand. An example of a simple chelating agent is ethylenediamine (NH_2 CH_2 CH_2 NH_2). Chelate rings are most stable when they have 5 or 6 members including the metal ion. The enhanced stability of chelate compounds is known as the chelate effect and mainly arises due to favourable entropy effect.

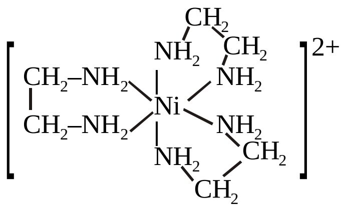
A single molecule of ethylenediamine can form two bonds to a transitionmetal ion such as nickel (II), NI^{2+}. The bonds form between the metal ion and the nitrogen atoms of - ethylenediamine. The nickel(II) ion can form six such bonds (coordination number 6), so a maximum of three ethylenediamine molecules can be attached to one Ni^{2+} ion.



chelate with one ethylenediamine ligand

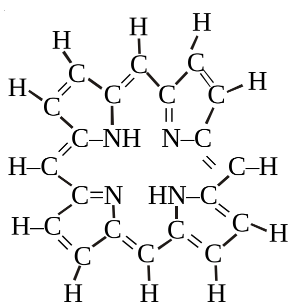


chelate with two ethylenediamine ligands

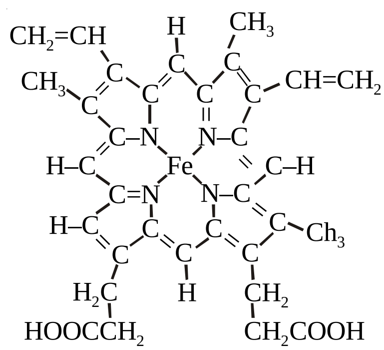


chelate with three ethylenediamine ligands

In the two structures on the left, the bonding capacity of the Ni^{2+} ion (6) is completed by water molecules. Each water molecule forms only one bond to Ni^{2+}, so water is not a chelating agent. Because the chelating agent is attached to the metal ion by several bonds, chelates tend to be more stable than complexes formed with monodentate ligands such as water.



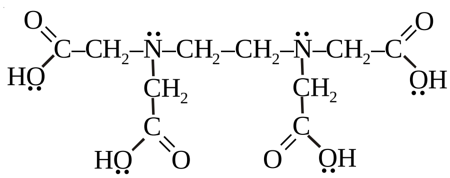
porphine



heme

Porphine is a chelating agent similar to ethylenediamine in that it forms bonds to a metal ion through nitrogen atoms. Each of the four nitrogen atoms in the center of the molecule can form a bond to a metal ion. Porphine is the simplest of a group of chelating agents called porphyrins. Porphyrins have a structure derived from porphine by replacing some of the outside hydrogen atoms with other groups of atoms. One important porphyrin chelate is heme, the central component of hemoglobin, which carries oxygen through the blood from the lungs to the tissues. Heme contains a porphyrin chelating agent bonded to an iron(ll) ion. Iron, like nickel, can form six bonds. Four of these bonds tie it to the porphyrin. One of iron's two remaining bonds holds an oxygen molecule as it is transported through the blood. Chlorophyll is another porphyrin chelate. In chlorophyll, the metal at the center of the chelate is a magnesium ion.

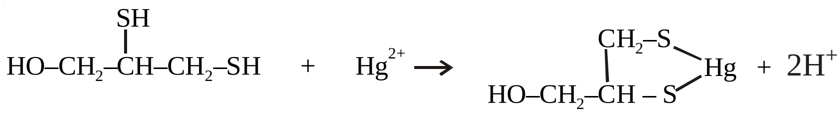
Chlorophyll, which is responsible for the green color of plant leaves, absorbs the light energy that is converted to chemical energy in the process of photosynthesis. Another biologically significant chelate is vitamin B-12. It is the only vitamin that contains a metal, a cobalt(ll) ion bonded to a porphyrin-like chelating agent. As far as is known, it is required in the diet of all higher animals. It is not synthesized by either higher plants or animals, but only by certain bacteria and molds. These are the sources of the B-12 found in animal products. Because vitamin B-12 is not found in higher plants, vegetarians must take care to include in their diets foods or supplements that contain the vitamin. A chelating agent of particular economic significance is ethylenediaminetetraacetic acid (EDTA).



ethylenediaminetetraacetic acid (EDTA)

EDTA is a versatile chelating agent. It can form four or six bonds with a metal ion, and it forms chelates with both transition-metal ions and main-group ions. EDTA is frequently used in soaps and detergents, because it forms complexes with calcium and magnesium ions. These ions are in hard water and interfere with the cleaning action of soaps and detergents. EDTA binds to them, sequestering them and preventing their interference. In the calcium complex. $[Ca(EDTA)]^{2-}$, EDTA is a tetradentate ligand, and chelation involves the two nitrogen atoms and two oxygen atoms in separate carboxyl ($-COC^{-}$) groups. EDTA is also used extensively as a stabilizing agent in the food industry. Food spoilage is often promoted by naturally-occurring enzymes that contain transition-metal ions. These enzymes catalyze the chemical reactions that occur during spoilage. EDTA deactivates these enzymes by removing the metal ions from them and forming stable chelates with them. It promotes color retention in dried bananas, beans, chick peas, canned clams, pecan pie filling, frozen potatoes, and canned shrimp. It improves flavor retention in canned carbonated beverages, salad dressings, mayonnaise, margarine, and sauces. It inhibits rancidity in salad dressings, mayonnaise, sauces, and sandwich spreads. EDTA salts are used in foods at levels ranging from 33 to 800 ppm. In other applications, EDTA dissolves the $CaCO_3$ scale deposited from hard water without the use of corrosive acid. EDTA is used in the separation of the rare earth elements from each other. The rare earth elements have very similar chemical properties, but the stability of their EDTA complexes varies slightly. This slight variation allows EDTA to effectively separate rare-earth ions. EDTA is used as an anticoagulant for stored blood in blood banks; it prevents coagulation by sequestering the calcium ions required for clotting. As an antidote for lead poisoning, calcium disodium EDTA exchanges its chelated calcium for lead, and the resulting lead chelate is rapidly excreted in the urine.

The calcium salt of EDTA, administered intravenously, is also used in the treatment of acute cadmium and iron poisoning. Dimercaprol (2.3-dimercapto-l-propanol) is an effective chelating agent for heavy metals such as arsenic, mercury, antimony, and gold. These heavy metals form particularly strong bonds to the sulfur atoms in dimercaprol.



dimercaprol

Dimercaprol was originally employed to treat the toxic effects of an arsenic-containing mustard gas called Lewisite [dichloro(2-chlorovinyl)arsine], which was used in World War I. The chelated metal cannot enter living cells and is rapidly excreted from the body. Since dimercaprol is water insoluble, it is dissolved in an oil base (often peanut oil) and injected intramuscularly).

3.9 Stereochemistry and isomerism of complexes:

Isomers are compounds that have the same chemical formulae but different arrangement of atoms. Because of the different arrangement of atoms, they differ in one or more physical or chemical properties. Two main types of isomerism are known among coordination compounds.

Each of which can be further subdivided.

1. Structural isomerism

A. Linkage isomerism : It arises in a coordination compound containing ambidentale ligands. A simple example is provided by complexes containing the thioeyanale ligand, NCS—, which may bind through the nitrogen to give M-NCS or through sulphur to give M—SCN. In complexes containing NO_2^- ligand, NO_2^- may bind through either O-atom or N-atom. Similarly, for $S_2O_3^{2-}$, the central metal may be coordinated either by S-atom or O-atom. Members of each pair of complex thus formed are linkage isomers to each other.

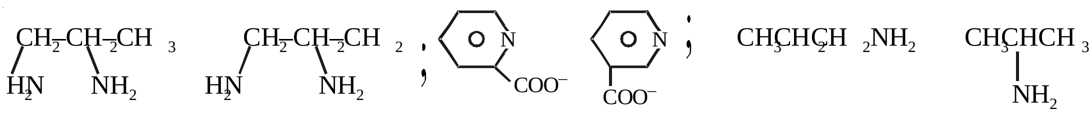
B. Coordination isomerism : This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. Both the cation and the anion in the complex compound are complexes themselves and there is an exchange of ligands between the two coordination spheres giving rise to coordination isomers. An example is provided by $[Co(NH_3)_6][Cr(CN)_6]$, in which the

NH_3 ligands are bound to Co^{3+} and the CN^- ligands to Cr^{3+}. In its coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$, the NH_3 ligands are bound to Cr^{3+} and the CN^- ligands to Co^3. $[Co(en)_3][Cr(C_2O_4)_3]$ and $[Co(en)_2(C_2O_4)][Cr(en)(C_2O_4)_2]$ are also coordination isomers (en = ethylenediamine, $C_2O_4^{2-}$ = oxalato).

C. Ionization isomerism : This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand in the inner coordination sphere and then become the counter ion. i.e. complexes which have the same empirical formula but give different ions in solution are ionisation isomers. An example is provided by the ionization isomers$[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$, $[Co(NH_3)_4ClNO_2]Cl$ etc.

D. Solvate isomerism : This form of isomerism is known as 'hydrate isomerism' in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example is provided by the aqua complex $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]CI_2.H_2O$ (grey-green) and $[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O$ (green)

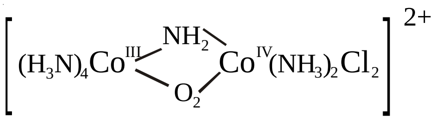
E. Ligand isomerism: Some ligands themselves are capable of existing as isomers such as 1,2-diaminopropane (pn) and 1,3-diaminopropane (tn). pyridine-2-carboxylate orpiconilate (pic) and pyridine-3-carboxylate or nicotinate (nic) n-propylamine (n-pram) and iso-propylamine (iso-pram) etc.



(pn) (tn) (pic) (nic) (n-pram) (iso-pram)

When these ligands form complexes, the complexes are isomers of each other e.g. $[Co(pn)_2Cl_2]^+$ and $[Co(tn)_2Cl_2]^+$ are ligand isomers.

F. Coordination position isomerism: In some polynuclear complexes, interchange of ligands between the metal centres within the coordination sphere gives rise to coordination position isomerism.



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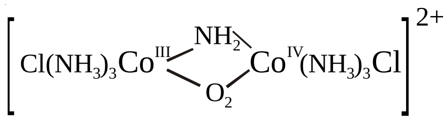


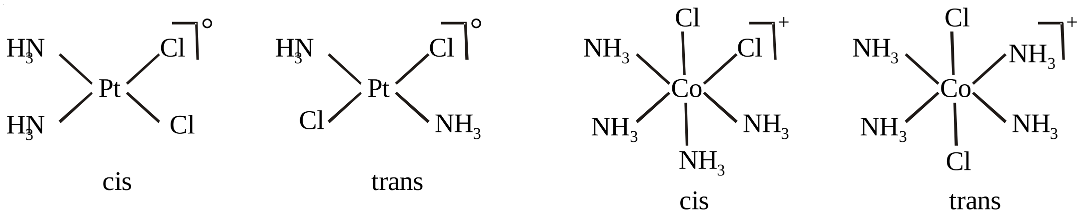
are

coordination position isomers.

2. Stereoisomerism

A. Geometrical isomerism : Geometrical isomers have identical empirical formula but differ in chemical and physical properties because of different arrangement of ligands.

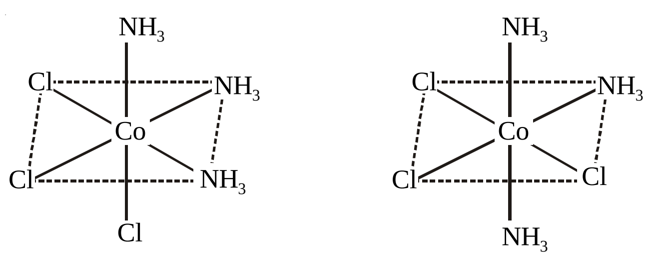
i) cis-trans isomerism : Here the isomers differ in the geometrical arrangement of the ligands around the central metal atom or ion. The isomer will be named eis if similar type of ligands occupy positions adjacent to each other and if the similar type of ligands occupy positions diagonally opposite to each other, the isomer is named trans. **Example:** $[Co(NH_3)_4Cl_2]$ and $[pt (NH_3)_2Cl_2]$.



Geometrical isomers (cis and trans)

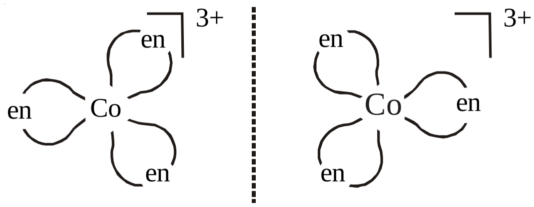
Geometrical isomerism cannot arise in a tetrahedral complex because in this geometry all positions are cis to each other. So this isomelism may occur in square planer (C.N = 4) and octahedral (C.N. = 6) complexes.

ii) fac-mer isomerism : An isomer becomes facial if three identical ligands occupy the vertices of a octahedron's triangular face (i.e. the ligands are at cis-positions). It becomes meridonial if these three ligands form together with the central atom a plane in the octahedron (i.e. when two identical ligands out of three are at the trans positions, it leads to mericlonial isomers since the three identical ligands are placed along the meridian. They are termed fac-or mer-isomers. Example: $[Co(NH_3)_3(NO_2)_3]$, $[Pt(NH_3)Br_3]^+$ $[Ru(H_2O)_3Cl_3]$ etc.



fac-isomer mer-isomer

B. Optical isomerism : Optical isomers are mirror images that cannot be superimposed on one another. These are called enantiomers.The moleeules or ions that cannot be superimposed are called chiral. The two forms are called dextro (d) and laexo (l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, *l* to the left). Optical isomerism is common in octahedral complexes involving didentate ligands. No mirror image isomerism is possible with tetrahedral and square plannar complexes. In tetrahidral arrangement, as all positions are equivalent, the images are superimposable. For square planar complexes, all the four ligands are in the same plane and hence have a plane of symmetry and are optically inactive. Example :



dextro mirror laevo

For octahedral complexes of the type $[Ma_2b_2c_2]$, $[Ma_2b_2cd]$, $[Ma_2bcde]$ and $[M_{abcdef}]$ (where a,b,c....etc are different monodentale ligands) optical isomers are possible. Octahedral complexes with symmetrical bidentate chelating ligands of the type $[M(AA)_3]^{n+/n-}$, cis-$[M(AA)_2ef]^{n\pm}$, cis-$[M(AA)_2e_2]^{n\pm}$, $[M(AA)c_2e_2]^{n\pm}$ are optically active. (AA = symmetrical bidentate i.e. similar donating groups).

3.10 Summary

Coordination compounds are of great importance. These compounds provide critical insights into the functioning and structures of vital components of biological systems. Coordination compounds also find extensive applications in metallurgical processes, analytical and medicinal chemistry. They are an important and challenging area of modern inorganic chemistry. During the last fifty years, advances in this area, have provided development of new concepts and models of bonding and molecular structure, novel breakthroughs in chemical industry and vital insights into the functioning of critical components of biological systems. The first systematic attempt at explaining the formation, reactions, structure and bonding of a coordination compound was made by A. Werner. His theory postulated the use of two types of linkages (primary and secondary) by a metal atom/ion in a coordination compound. In the modern language of chemistry these linkages are recognised as the ionisable (ionic) and non-ionisable (covalent) bonds, respectively. Using the property of isomerism, Werner predicted the geometrical shapes of a large number coordination entities. The stability of coordination compounds is measured in terms of stepwise or formation) constants (K) or overall stability constans (β). The stabilisation of coordination compound due to chelation is called the chelate effect. The explanation and interactions of metal ions and ligands and EAN calculation techniques have also been provided in this chapter. Different types of isomerism possible in the coordination compounds are also discussed.

3.11 Selt Assessment Questions

1. Write the differences between complex salts and double salts.
2. Give examples of complex salts and double salts.
3. State and explain Werner's theory.
4. Write the postulates of Werner's theory.
5. What do you mean by EAN rule?
6. Calculate EAN of $Ni(CO)_4$; $[Cu(NH_3)_4]^{2+}$; $Pt(NH_3)_4]^{2+}$
7. State the exceptions of EAN rule.
8. What do you mean by the term ligand?
9. What are monodentate ligands? Give examples.
10. What are bidentate ligands? Give examples.
11. What are ambidentate ligands? Give examples.
12. What are polydentate ligands? Give examples.
13. Write the IUPAC names of—

    A. $[Pt(NH_3)_5Cl]Br_3$

    B. $[Pt(H_2NCH_2CH_2NH_2)_2Cl_2]Cl_2$

    C. $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$

    D. $K_4[Fe(CN)_6]$

    E. $Na_2[NiCl_4]$

    F. $Pt(NH_3)_2Cl_4$

G. $Fe(CO)_5$

14. How are overall and stepwise stability constant related?
15. What are chelates?
16. What do you mean by linkage isomerism?
17. What do you mean by coordination isomerism?
18. What do you mean by ionisation isomerism?
19. What do you mean by solvate isomerism?
20. What do you mean by cis-trans isomerism?
21. What do you mean by fac-mer isomerism?

Answer Key

1. See section 3.1	2. See section 3.1	3. See section 3.2
4. See section 3.2	5. See section 3.3	6. See section 3.3
7. See section 3.3	8. See section 3.4	9. See section 3.4
10. See section 3.4	11. See section 3.4	12. See section 3.4
13. See section 3.5	14. See section 3.6	15. See section 3.7
16. See section 3.8	17. See section 3.8	18. See section 3.8
19. See section 3.8	20. See section 3.8	21. See section 3.8

3.12 Further Reading

1. G. B. Kauffman, Classics in Coordination Chemistry, Dover Pub. New York (1995).
2. P. R. Shukla, Advance Coordination Chemistry Himalaya Publishing House.
3. G. A. Lawrance, Introduction to coordination Chemistry, A John Wiley and Sons Ltd., Publication.
4. Basic Inorganic Chemistry, Cotton, Wilkinson, Gaus 3rd Ed. John Wiley and Sons Inc., 2004.
5. Fundamental Concepts of Inorganic Chemistry A. K. Das and M. Das volume 2, First Ed., 2015.

Unit 4 ❑ Coordination Chemistry-II

4.0 Objectives

After reading this unit you can be able to know—

* Structure and bonding of Coordination Compounds.
* Elementary idea about crystal field theory.

* Jahn Teller theorem and its applications.
* Idea about a^{-} and H^{-}-bonding in octahedral complexes.
* Concept about charge transfer transitions L-S coupling and R-S ground state terms.
* Idea about Orgel diagrams.

4.1 Introduction

In order to explain the nature of Coordination Compoundsgenerally three theoriesare considered—Valence bond theory (VBT), crystal field theory (CFT), and molecular orbital theory (MO). The bonding theory are useddescribed molecules and ions was the VBT which is indeed an essential bonding theory describe the vast majority of molecules and during the year 1930-1950. This theory is based on the orbital overlap model and was developed by pauling. The inadequacies of VBT arises in case of electron deficient molecule to explain the colour of Coordination complexes. Thus crystal field theory gained ground. The ligand field and crystal field theory were first developed by H. Bethe. The crystal theory strictly valid for ionic complexes, on the otherhand molecular theory explains the covalent bonding in the complexes.

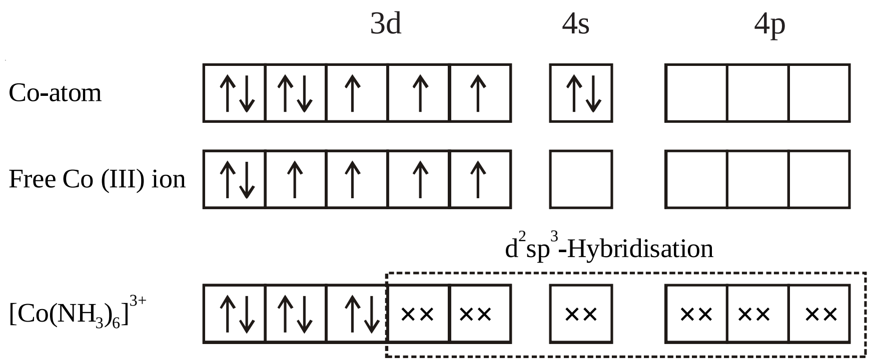
4.2 Structure and bonding of coordination compounds on the basis of Valence Bond Theory (VBT) and its limitations

The idea that atoms form covalent bonds by sharing pairs of electrons was first proposed by G. N. Lewis in 1902. It was not until 1927, however, that Walter Heitler and Fritz London showed how the sharing of pairs of electrons holds a covalent molecule together. The Heitler-London model of covalent bonds was the basis of the valence-bond theory. The last major step in the evolution of this theory was the suggestion by Linus Pauling that atomic orbitals mix to form hybrid orbitals, such as the sp, sp^2, sp^3, dsp^2, and $d^2 sp^3$ orbitals.

According to this theory, the metal atom or ion under the influence of ligands can use its (ns, np or (n–1)d, ns, np, nd orbitals for hybridization to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and so on. These hybridized orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

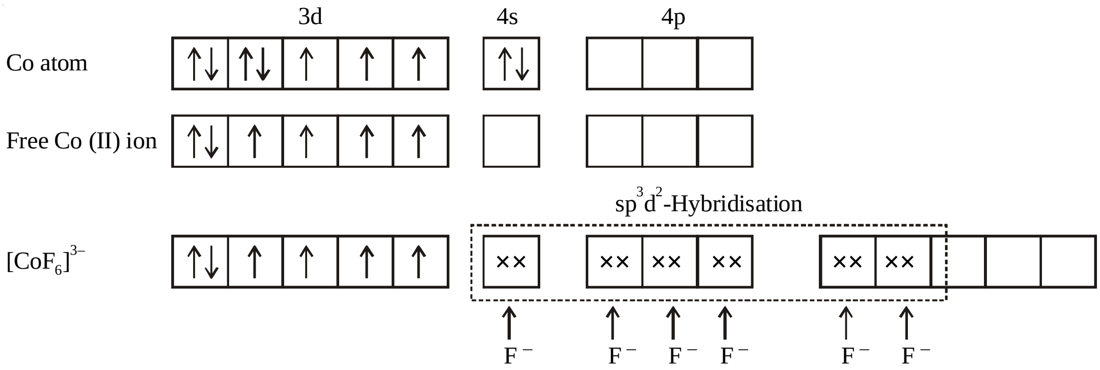
Coordination Number	Type of hybridisation	Distribution of hybrid orbitals in space	Examples
4	sp^3	Tetrahedral	$[Ni(CO)_4]$
4	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$
5	sp^3d	Trigonal bipyramidal	$[Fe(CO)]_5$
6	d^3sp^3	Octahedral	$[Co(NH_3)_6]^{3+}$
6	sp^3d^2	Octahedral	$[CoF_6]^{3-}$

It is usually possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis of the valence bond theory. Pauling has made a use of magnetic measurements to findout the number of unpaired electrons in a complex. According to him, the number of unpaired electrons and geometries of the complexes are related to each other (Magnetic criterion of Bond Type). In the diamagnetic octahedral complex. $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the outer electronic configuration $3d^6 4s^\circ$. Six pairs of electrons, one from each NH_3, molecule, occupy the six hybrid orbitals. The complex has octahedral geometry and is diamagnetic because of the absence of unpaired electrons.

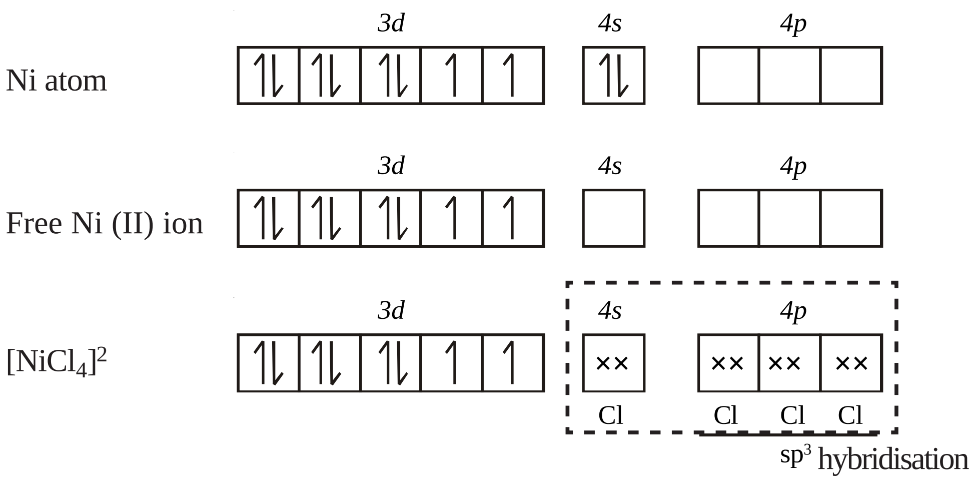


×× denotes electron pairs donated by ligands

In the formation of this complex, since the inner d orbital (3d) is used in hybridisation. the complex, $[Co(NH_3)_6]^{3+}$ is called an inner orbital or low spin or spin paired complex. The paramagnetic octahedral complex, $[CoF_6]^{3-}$ uses outer orbital (4d) in hybridisation (sp^3d^2). It is thus called outer orbital or high spin or spin free complex.

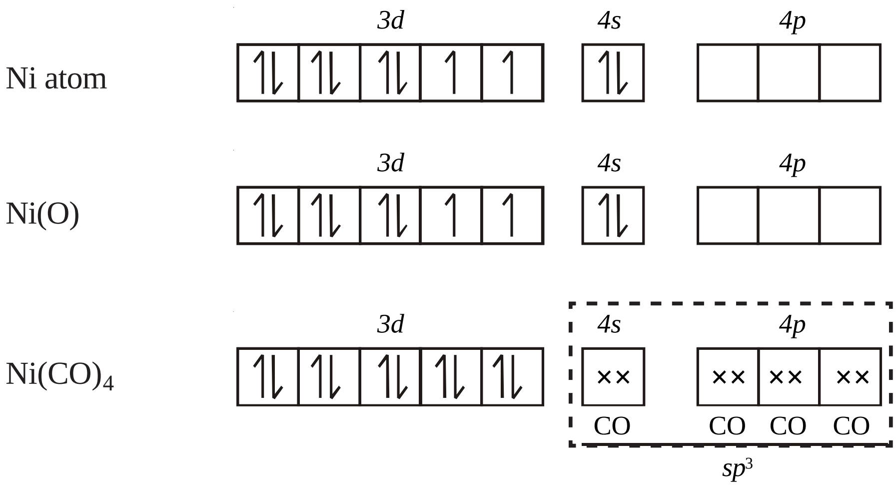


In tetrahedral complexes one s and three p orbitals are hybridised to form four equivalent orbitals oriented tetrahedrally. This is illustrated below for $[NiCl_4]^{2-}$. Here nickel is in +2 oxidation state and the ion has the outer electronic configuration $3d^8 4s°$. The hybridisation scheme is as shown in the diagram below. Each Cl^- ion donates a pair of electrons.

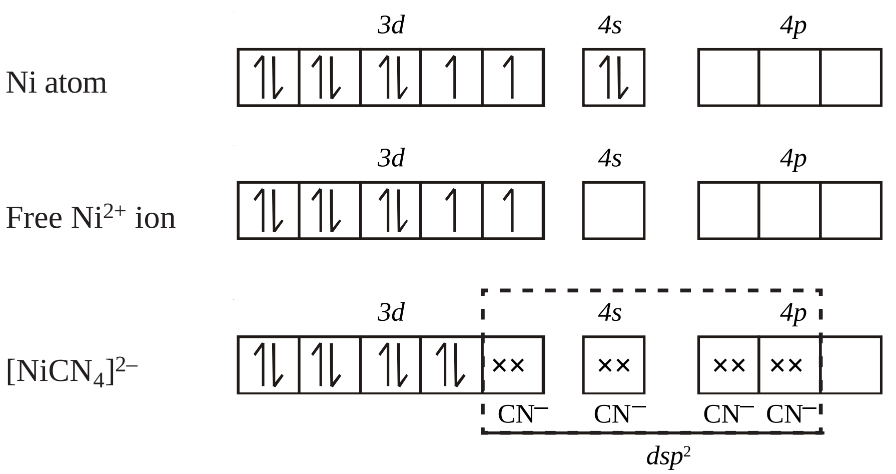


The compound is paramagnetic since it contains two unpaired electrons. Similarly, $[Ni(CO)_4]$ has tetrahedral geometry but is diamagnetic since nickel is in zero oxidation state and contains no unpaired electrons. In the square planar complexes, the hybridisation involved is dsp^2. An example is $[Ni(CN)_4]^{2-}$. Here nickel is in +2 oxidation state and has the outermost electronic configuration $3d^8 4s^0$. Each of the hybridised orbitals receives a pair of electrons from a cyanide ion. The compound is diamagnetic as evident from the absence of unpaired electron.

$Ni(CO)_4$



$[Ni(CN)_4]^{2-}$



It is important to note that the hybrid orbitals do not actually exist. In fact, hybridisation is a mathematical manipulation of wave equation for the atomic orbitals involved.

Limitations of Valence bond theory:

While the VB theory, to a larger extent, explains the formation, structures and magnetic behaviour of coordination compounds, it has many limitations:

1. It involves a number of assumptions.
2. It does not give quantitative interpretation of magnetic data.
3. Octahedral (d^2sp^3) or sp^3d^2), tetrahadral (sp^3) and square planar (dsp^2) complexes of d^1, d^2, d^3 and d^9 have the same number of unpaired electrons and hence cannot be distinguished from each other merely on the basis on number of unpaired electrons.
4. It cannot explain why square planar complexes like $[Cu(NH_3)_4]^{2+}$ (d^9 system) and inner orbital Co^{+2} (d^7) complexes are not reducing agents although in both cases promotion of a non-bonding d-electron to some higher energy level (presumably 5s) is required.
5. Too much stress has been laid on the metal ion while the importance of ligands are ignored.
6. It does not explain the colour exhibited by coordination compounds.
7. It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination eompounds and cannot explain reaction rates and mechanism of reactions.
8. It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes. It does not distinguish between weak and strong ligands.

4.3 Elementary idea about Crystal Field Theory (CFT)

This theory (CFT) largely replaced VB Theory for interpreting the chemistry of coordination compounds. It was proposed by the physicist Hans Bethe in 1929. Subsequent modifications were proposed by J. H. Van Vleck in 1935 to allow for some covalency in the interactions. These modifications are often referred to as Ligand Field Theory. The interactions between the metal ion (positively charged) and the ligands are purely electrostatic (ionic). The ligands are regarded as point charges or point dipoles is the ligand is negatively charged, ion-ion interaction. If the ligand is neutral, ion-dipole interaction. The electrons on the metal are under repulsion from those on the ligands. It is these repulsive forces that are responsible for causing the splitting of d-orbitals of the metal centre. According to crystal field theory, the interaction between a transition metal and ligands arises from the attraction between the positively charged metal cation and the negative charge on the non-bonding electrons of the ligand. The theory is developed by considering energy changes of the five degenerate d-orbitals upon being surrounded by an array of point charges consisting of the ligands. As a ligand approaches the metal ion or atom, the electrons from the ligand will be closer to some of the d-orbitals and farther away from others, causing a loss of degeneracy. The electrons in the d-orbitals and those in the ligand repel each other due to repulsion between like charges. Thus the d-electrons closer to the ligands will have a higher energy than those further away which results in the d-orbitals splitting in energy.

Factors affecting crystal field splitting:

1. The nature of the metal ion.
2. The metal's oxidation state. A higher oxidation state leads to a larger splitting relative to the spherical field.
3. The arrangement of the ligands around the metal ion.
4. The coordination number of the metal (i.e. tetrahedral, octahedral...)
5. The nature of the ligands surrounding the metal ion. The stronger the effect of the ligands, the greater the difference between the high and low energy d orbitals.

The most common type of complex is octahedral in which six ligands form the vertices of an octahedron around the metal centre. The five d-orbitals have been divided into two groups in octahedron symmetry.

(i) Group that has the orbitals with their lobes along the axes (axial orbitals). Obviously these are dz^2 and $d_{x^2-y^2}$ and forms a doubly degenerate state.

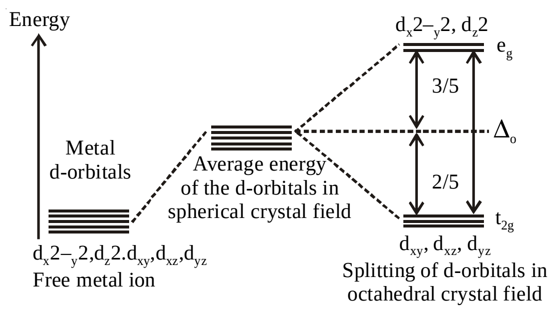
ii) Group that has the orbitals whose lobes between the axes (non-axial orbitals) They are dxy, dxz, dyz.

In octahedral symmetry, therefore, the d-orbitals split into two sets with an energy difference, Δ_{oct} (the crystal-fteld splitting parameter) where the dxy, dxz and dyz orbitals will be lower in energy than the dz^2 and dx^2-y^2, which will have higher energy, because the former group is farther from the ligands than the latter and therefore experiences less repulsion. The three lower-energy orbitals are collectively referred to as t_2g and the two higher-energy orbitals as eg (These labels are based on the theory of molecular symmetry). The crystal field splitting energy, Δ_{oct} (Δ_o) is also denoted by an energy term, $10Dq_0$.

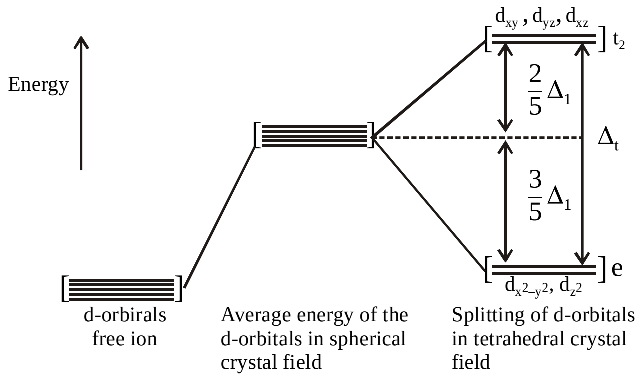
If we consider the splerical destribution of ligand charges, then the barycentre (i.e. centre of gravity) of the d-orbitals will be displaced maintaining the degeneracy. If the same amount of spherical charge is redistributed at the six corners of a regular octahedron (with same metal-ligand distance) then the barycentre will be the same as in the case of spherically symmetrical field. Thus the mere redistribution of the spherical charge cannot alter the energy of the system i.e. the barycentre or centre of gravity of d-orbital.

So the following condition is obeyed:

Destabilisation caused by eg set ($d_z{}^2$and $d_{x^2-y^2}$) = Stabilisation caused by t_2g set (dxy, dxz, dyz). If the splitting energy is taken as 10 Dq_0, each t_2g electron (in any of the three dgenerate orbitals) is stabilised by 4 Dq_0 and each eg electron (in any of the two degenerate orbitals) destabilised by 6 Dq_0 with respect to the energy of the electrons in the pre-splitting condition. Similarly it can be known that if Δ_0 is taken as the splitting energy, then the t_2g set is stabilised by $\frac{2}{5}\Delta_0$ (0.4 Δ_0) and eg set destabilised by $\frac{3}{5}\Delta_0$ (0.6 Δ_0) relative to the d-orbitals in the pre-splitting condition (i.e. barycentre).



Tetrahedral complexes are the second most common type; here four ligands form a tetrahedron around the metal centre. In a tetrahedral crystal field splitting, the d-orbitals again split into two groups, with an energy difference of Δtet (Δt). The lower energy orbitals will be d_z2 and d_x2-$_y2$. and the higher energy orbitals will be d_{xy}. d_{xz} and d_{yz} opposite to the octahedral ease. The geometry of tetrahedron within a cube kave the four negative ligands at the alternate corners of the cube and are lying between the three axes (x,y,z). The dxy, dxz, dyz orbitals have lobes between the axes and face the ligands more directly than dz^2 and $dx^2–y^2$. So they face greater repulsion from ligands than the other two. So the former three orbitals will be raised in energy (t_2 set in tetrahedral symmetry) and the latter two (e set) will be stablished with respect to the barycentre. Furthermore, since the ligand electrons in tetrahedral symmetry are not oriented directly towards the d-orbitals, the energy splitting will be lower than in the octahedral i.e. $\Delta_t < \Delta_0$. It can be shown that $\Delta_t = {}^4/_9\ \Delta_0$. 'g' is omitted in tetrahedral case as this geometry do not have a centre of symmetry. Square planar and other complex geometries can also be described by CFT.



The size of the gap Δ between the two or more sets of orbitals depends on several factors, including the ligands and geometry of the complex. Some ligands always produce a small value of Δ, while others always give a large splitting. The reasons behind this can be explained by ligand field theory.

Spectrochemical Series:

The spectrochemical series is an empirically-derived list of ligands ordered by the size of the splitting Δ that they produce (small Δ to large Δ):

I^- Br^- < S^{2-} < SCN^- < Cl^- NO_3^- < N_3^- < F^- < OH^- < $C_2O_4^{2-}$ < H_2O < NCS^- < CH_3CN < py < NH_3 < en < 2,2-bipyridine < phen < NO_2^- < PPh_3 < CN^- < CO

It is useful to note that the ligands producing the largest splitting are those that can engage in metal to ligand back-bonding. The oxidation state of the metal also contributes to the size of Δ between the high and low energy levels. As the oxidation state increases for a given metal, the magnitude of Δ increases. A V^{3+} complex will have a larger Δ than a V^{2+} complex for a given set of ligands, as the difference in charge density allows the ligands to be closer to a V^{3+} ion than to a V^{2+} ion. The smaller distance between the ligand and the metal ion results in a larger Δ because the ligand and metal electrons are closer together and therefore repel more. Ligands which cause a large splitting Δ of the d-orbitals are referred to as strong-field ligands such as CN^- and CO from the spectrochemical series. In complexes with these ligands, it is unfavourable to put electrons into the high energy orbitals. Therefore, the lower energy orbitals are completely filled before population of the upper sets starts according to the Aufbau principle. Complexes such as these are called "low spin" (spin-paired complexes). For example. NO_2^- is a strong-field ligand and produces a large Δ. The octahedral ion $[Fe(NO_2)_6]^{3-}$, which has 5 d-electrons. would have the all the five electrons in the t_2g level. This low spin state therefore does not follow Hund's rule. Conversely, ligands (like I^- and Br^-) which cause a small splitting Δ of the d-orbitals are referred to as weak-field ligands. In this case, it is easier to put electrons into the higher energy set of orbitals than it is to put two into the same low-energy orbital, because two electrons in the same orbital repel each other. So. one electron is put into each of the five d-orbitals in accordance with Hund's rule, and "high spin" complexes (or spin-tree complexes) are formed before any pairing occurs. For example, Br^- is a weak-field ligand and produces a small Δoct. So, the ion $[FeBr_6]^{3-}$, again with five d-electrons, would have all five orbitals (t_2g and eg) singly occupied.

In order for low spin to occur, the energy cost of placing an electron into an already singly occupied orbital must be less than the cost of placing the additional electron into an lg orbital at an energy cost of Δ. As noted above, lg refers to the dz^2 and $dx^2–y^2$ which arc higher in energy than the t_2g in octahedral complexes. If the energy-required to pair two electrons is greater than Δ, the energy cost of placing an electron in an lg is more appropriate and a high spin complex is formed. The crystal field splitting energy for tetrahedral metal complexes (four ligands) is referred to as Δtet. (Δt) and is roughly equal to 4/9Δoct (for the same metal and same ligands). Therefore, the energy required to pair two electrons is typically higher than the energy required for placing electrons in the higher energy orbitals. Thus, tetrahedral complexes are usually high-spin.

Thus if $\Delta o < P$, (P=pairing energy) the fourth electron enters one of the eg orbitals giving the configuration $t_2g^3eg^1$. Ligands for which $\Delta o < P$ are known as weak field ligands and form high spin complexes, whereas, if $\Delta o > P$, it becomes more energetically favourable for the fourth electron to occupv a t_2g orbital resulting in a configuration $t_2g^4eg^\circ$. Ligands which produce this effect are known as strong field ligands and form low spin complexes or spin-paired complexes.

Distribution of electrons in octahedral field in presence of strong field and weak field ligands:

The use of these splitting diagrams can aid in the prediction of magnetic properties of coordination compounds. A compound that has unpaired electrons in its splitting diagram will be paramagnetic and will be attracted by magnetic fields, while a compound that lacks unpaired electrons in its splitting diagram will be diamagnetic and will be weakly repelled by a magnetic field.The crystal field stabilization energy (CFSE) is the stability that results from placing a transition metal ion in the crystal field generated by a set of ligands. It arises due to the fact that when the d-orbitals are split in a ligand field (as described above), some of them become lower in energy than before with respect to a spherical field known as the barycenter in which all five d-orbitals are degenerate.

For example, in an octahedral case, the t_2g set becomes lower in energy than the orbitals in the barycenter. As a result of this, if there are any electrons occupying these orbitals, the metal ion is more stable in the ligand field relative to the barycenter by an amount known as the CFSE (Crystal Field Stabilisation Energy).

Conversely, the eg orbitals (in the octahedral case) are higher in energy than in the barycenter, so putting electrons in these reduces the amount of CFSE.

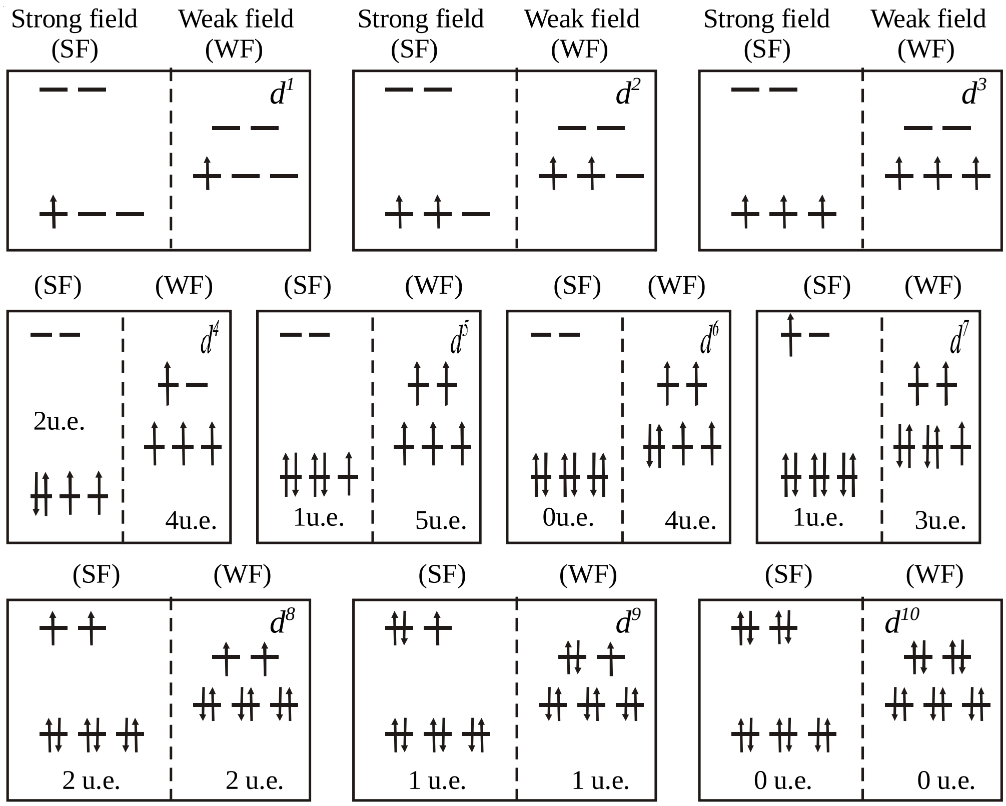
Examples: For d' metal ion in octahedral field, the electron occupies a t_2g orbital with an energy of $-0.4\ \Delta_0$ (–4Dq) relative to the barycentre of d-orbitals, (negative sign denotes stablisation relative to barycentre). The complex can thus he said to be stabilised to the extent of $0.4\ \Delta_0$ or 4Dq.

For d^4 (high spin) $t_2g^3eg^1$ configuration, CFSE = $(3\times-0.4\Delta_0)-(1\times0.6\Delta_0)=0.6\Delta_0$. For d^4 (low spin) t_2g^4 configuration, CFSE = $(4\times-0.4\Delta_0) = -1.6\Delta_0$ (or, $-4\Delta_0)=16\Delta_0$.

The CFSE can be stated as $-0.6\Delta_0$ or, $-1.6\Delta_0$ (negative sign in dicates stabilisation) of by CFSE = $0.6\Delta_0$ or $1.6\Delta_0$ denotes (with nonegative sign) stabilisation by that amount.

It pairing is considered, pairing of electrons would destabilise the system because of electronic repulsion and CFSE should be $1.6\ \Delta_0$ – P or 16 Dq – P]. If CFSE is denoted by negative sign or $-1.6\Delta_0$ (–16Dq) then CFSE is given as $-1.6\Delta_0$ + P (–16 Dq + P). Positive sign denotes destabilisation.

When calculating CFSE, for weak field cases, comparison is made with free ion configuration, so number of electron pairs are same in both cases and P (pairing energy) can be omitted. For strong field cases, comparison is made with weak field (i.e. free ion) and extra pairs are subtracted from CFSE. If CFSE is stated as positive and added if CFSE is stated as negative. For example high spin d^7 metal ion has configuration $t_2g^5eg^2$ and CFSE = $0.8\Delta_0$ – 2P (or sometimes $-0.8\ \Delta_0$ + 2P). Low spin d^7 will have the configuration $t_2g^6eg^1$ and CFSE = $1.8\Delta_0$ – 3P (or $-1.8\Delta_0$ + 3P). In comparison to WF case (or free ion) SF configuration has one extra 'pair' of electrons. So the CFSE can be written as $1.8\Delta_0$ – P (or – $1.8\Delta_0$ + P). (Note in terms of Dq, the CFSE's will be –8 Dq + 2P–18 Dq + 3p (or 8 Dq – 2P, 18 Dq – 3P) and so on.



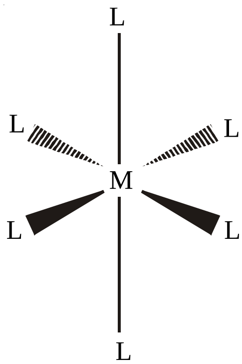
u.e. = unpaired electrons

	Octahedral field				Tetrahedral field		
	High spin		Low spin		High spin		Low spin
d-system	**Configu-ration**	**CFSE**	**Configu-ration**	**CFSE**	**Configu-ration**	**CFSE**	
d^1	$t_2g^1eg^0$	$0.4\ \Delta_0$	$t_2g^1eg^0$	$0.4\ \Delta_0$	$e^1t_2^0$	$0.6\ \Delta t$	
d^2	$t_2g^2eg^0$	$0.8\ \Delta_0$	$t_2g^2eg^0$	$0.8\ \Delta_0$	$e^2t_2^0$	$1.2\ \Delta t$	
d^3	$t_2g^3eg^0$	$1.2\ \Delta_0$	$t_2g^3eg^0$	$1.2\ \Delta_0$	$e^2t_2^1$	$0.8\ \Delta t$	
d^4	$t_2g^3eg^1$	$0.6\ \Delta_0$	$t_2g^4eg^0$	$1.6\ \Delta_0$	$e^2t_2^2$	$0.4\ \Delta t$	

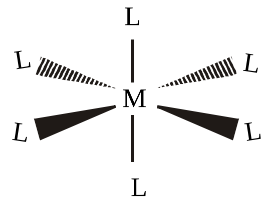
d^5	$t_2g^3eg^2$	$0.0\ \Delta_0$	$t_2g^5eg^0$	$2.0\ \Delta_0$	$e^2t_2{}^3$	$0.0\ \Delta_t$
d^6	$t_2g^4eg^2$	$0.4\ \Delta_0$	$t_2g^6eg^0$	$2.4\ \Delta_0$	$e^3t_2^3$	$0.6\ \Delta_t$
d^7	$t_2g^5eg^2$	$0.8\ \Delta_0$	$t_2g^6eg^1$	$1.8\ \Delta_0$	$e^4t_2{}^3$	$1.2\ \Delta_t$
d^8	$t_2g^6eg^2$	$1.2\ \Delta_0$	$t_2g^6eg^2$	$1.2\ \Delta_0$	$e^4t_2{}^4$	$0.8\ \Delta_t$
d^9	$t_2g^6eg^3$	$0.6\ \Delta_0$	$t_2g^6eg^3$	$0.6\ \Delta_0$	$e^4t_2{}^5$	$0.4\ \Delta_t$
d^{10}	$t_2g^6eg^4$	$0.0\ \Delta_0$	$t_2g^6eg^4$	$0.0\ \Delta_0$	$e^4t_2^6$	$0.0\ \Delta_t$

4.4 Jahn Teller theorem and applications

Hermann Jahn and Edward Teller in 1937, postulated a theorem stating that "stability and degeneracy are not possible simultaneously unless the molecule is a linear one," with regard to its electronic state. This leads to a break in degeneracy which stabilizes the molecule and by consequence, reduces its symmetry. Since 1937, the theorem has been revised which Housecraft and Sharpe have eloquently phrased as "any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy. "This is most commonly observed with transition metal octahedral complexes. In the octahedral system, if the two trans ligands lying along the Z-axis are compressed or elongated compared to other four ligands in the xy-plane, a tetragonally distorted octahedrons are obtained. However, it can be observed in tetrahedral compounds as well. The Jahn-Teller effect is a geometric distortion of a non-linear molecular system that reduces its symmetry and energy. This distortion is typically observed among octahedral complexes where the two axial bonds can be shorter or longer than those of the equatorial bonds. This effect can also be observed in tetrahedral compounds. This effect is dependent on the electronic state of the system. For a given octahedral complex, the five d atomic orbitals are split into two degenerate sets when constructing a molecular orbital diagram. These are represented by the sets' symmetry labels: t_2g (d_{xz}, d_{yz}, d_{xy}) and eg (d_{z^2} and $d_{x^2-y^2}$). When a molecule possesses a degenerate electronic ground state, it will distort to remove the degeneracy and form a lower energy (and by consequence, lower symmetry) system. The octahedral complex will either elongate or compress the ligand bonds.

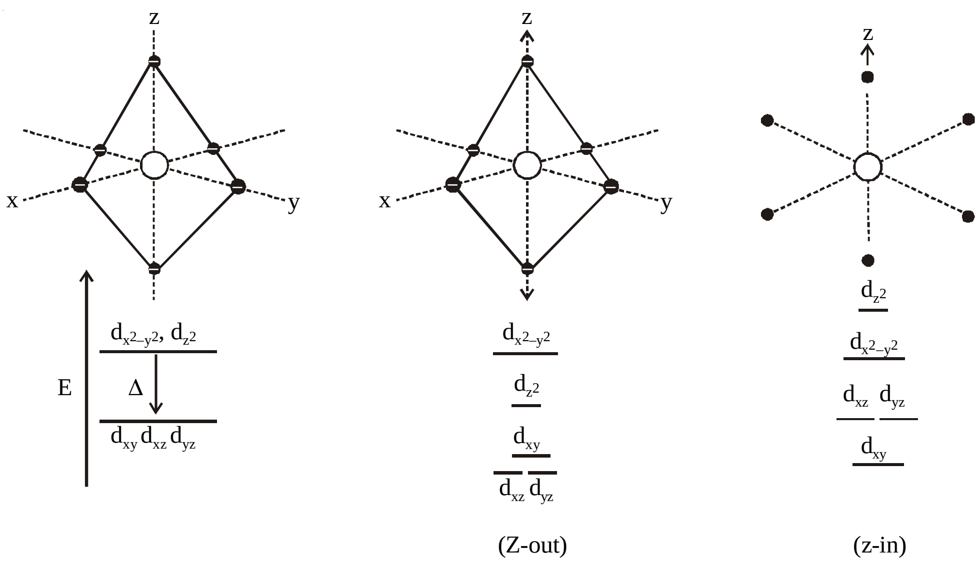


Elongated

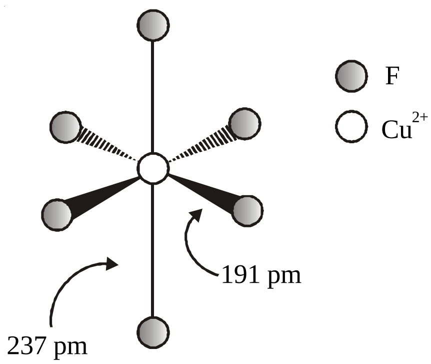


Compressed

When an octahedral complex exhibits elongation (z-out), the axial bonds are longer than the equatorial bonds. For a compression (z-in) it is the reverse; the equatorial bonds are longer than the axial bonds. Elongation and compression effects are dictated by the amount of overlap between the metal and ligand orbitals. Thus, this distortion varies greatly depending on the type of metal and ligands. In general, the stronger the metal-ligand orbital interactions are, the greater the chance for a Jahn- Teller effect to be observed. Thus distortion will occur if only the splitted energy levels can yield an additional stabilisation through distortion. For octahedral complexes, if distortion occurs due to uneven occupancy of electrons in the eg set (eg^1or eg^3), it is more severe than cases where uneven occupancy is in t_2g set, since the interaction of electrons with legands is more direct (along the axis) in the eg set. For tetrahedral complexes, the J.T. elistortion is significant if t_2 set is unsymmetrically filled up.



Elongation Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals with a z component, (due to lower rupulsion with ligands) while the orbitals without a z component are destabilized (higher in energy). This is due to the dxy and $d_{x^2-y^2}$ orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the $d_{x^2-y^2}$ orbital is antibonding, it is expected to increase in energy due to elongation. The d_{xy} orbital is still nonbonding, but is destabilized due to the interactions. J.T. distortion in octahendral geometry. d^1, d^4 (h.s.), d^7 (l.s.), d^9, d^6 (h.s.) Tetrahedral: d^3, d^4, d^8, d^9 occupation of electrons in t_2 level). Jahn-Teller elongations are well-documented for copper(ll) (d^9), octahedral compounds. A classic example is that of copper(II) fluoride. Some examples of Jahn-Teller distorted complexes are K_2CuF_4 and $KCuAlF_6$. ln the former, four F atoms are at 191 pm and two F atoms are at 237 pm and in the latter, two F atoms are at 188 pm and four F atoms are at 220 pm.



4.5 Limitations of CFT

The crystal field theory suffers from the following limitations:

1. The CFT cannot explain the colour of substances with a full or empty d orbital.$KMnO_4$ is one such substance in which the d orbital is empty.
2. There is another kind of electron transfer called Charge Transfer(CT) which is more powerful than d-d transfer and is between metal and ligand. This type of electron transfer is not covered in crystal field theory and can only be explained using MOT.
3. It treats metal ligand interactions as purely ionic. Hence it cannot be used for sulfides as sulfides form mostly covalent bonds.

4. It cannot satisfactorily explain chemical bonding. Complexes may also be formed between neutral metal atoms and neutral or cationic ligands. Crystal Field Theory is poorly suited to explain such interactions.

5. Crystal Field Theory fails in explaining why a neutral ligand such as CO can cause a very large crystal field splitting. as it does not consider formation of π-bonds in complexes. Molecular Orbital Theory explains why the CO ligand leads to a higher crystal field splitting.

6. It does not explain why the anionic ligands are present at low end of the spectrochemical series, and why H_2O, a neutral ligand, appears in the spectrochemical series as a stronger ligand than OH^-.

4.6 Nephelauxetic effect

Nephelauxetic effect (β)generally denotes the decrease in the Racah interelectronic repulsion parameter (B) which indicates that in a complex there is less repulsion between the two electrons in a given doubly occupied metal d-orbital than there is in the respective M^{n+} gaseous metal ion, which in turn implies that the size of the orbital is larger in the complex. This electron cloud expansion effect may occur for one (or both) of two reasons. One is that the effective positive charge on the metal has decreased. Because the positive charge of the metal is reduced by any negative charge on the ligands, the d-orbitals can expand slightly. The second is the act of overlapping with ligand orbitals and forming covalent bonds increases orbital size, because the resulting molecular orbital is formed from two atomic orbitals. The name "nephelauxetic" comes from the Greek for ‘cloud-expanding’. The presence of this effect brings out the disadvantages of crystal field theory, as this accounts for somewhat covalent character in the metal-ligand interaction.

The reduction of B from its free ion value is given as $\beta = \dfrac{B_{complex}}{B_{free\ \ ion(gaseous)}}$

Experimentally, it is observed that size of the nephelauxetic parameter always follows a certain trend with respect to the nature of the ligands present. The value depends on the extent of covalency in metal-ligand bond and depends on the nature of both the metal and the ligand.

The metal ions are arranged in terms of nephelauxetic effect as follows (with a particular ligand):

Mn(II) <Ni(ll) ≈ Co(ll) < Mo(II) < Re(IV) < Fe(lll) < Ir(IIl) < Co(lll) < Mn(IV)

The ligands are arranged in terms of increasing nephelauxetic effect as follows.

$$F^- < H_20 < NH_3 < en < NCS^- < CI^- < CN^- < Br^- < N_3 < 1^-$$

β can never be greater than unity (β ≤ 1). β = 1 indicates 100% ionic interaction in the metal-ligand. For non-polarisable ligands like F^-, β is close to unity and for polarisable ligands as I^-, S^{2-}β is less than unity. The nephelauxetic series of metal ions also depends on the covalent bond forming power of the metal ions.

4.7 Stabilisation of unusual high and low oxidation states of 3d transition elements

The chemical environment required to stabilise high oxidation states from that required in stablising low oxidation states : Metal ions in higher oxidation states become oxidising, and so for stabilisation of the higher state, the surrounding environment must be resistant to prevent oxidation. The ligands must be non-oxidisable and non-potarisable. Low oxidation states (can be zero or even negative) are sensitive to oxidation by atmospheric O_2 or ligands. Synthesis of such compounds are carried out in O_2 free environment. The ligands should produce a reducing environment around the metal centre. So large ligands as I^-, S^{2-} etc. are suitable for stabilising low oxidation states. For the stable halides of the 3d series of transition metals, the highest oxidation numbers are achieved in TiX_4 (tetrahalides), VF_5 and CrF_6. The +7 state for M_n is not represented in simple halides but MnO_3F is known, and beyond Mn no metal has a trihalide except FeX_3 and CoF_3. The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in the case of CoF_3, or higher bond enthalpy terms for the higher covalent compounds, e.g., VF_5 and CrF_6. Although V^{+5} is represented only by VF_5, the other halides, however, undergo hydrolysis to give oxohalides, VOX_3. Another feature of fluorides is their instability in the low oxidation states e.g., VX_2 (X = Cl, Br or I) and the same applies to CuX. F^- is the least polarisable ion.

Oxidation number		+6	+5	+4	+3	+2	+ 1
Groups	4	-	-	TiX_4	TiX_3	TiX_2	-
	5	-	VF_5	VX_4	VX_3	VX_2	-
	6	CrF_6	CrF_5	CrX_4	CrX_3	CrX_2	-

	7	-	-	MnF_4	MnF_3	MnX_2	-
	8	-	-	-	FeX_3	FeX_2	-
Groups	9	-	-	-	CoX_3	CoX_2	-
	10	-	-	-	-	NiX_2	-
	11	-	-	-	-	CuX_2	CuX
	12	-	-	?	"	ZnX_2	-

On the other hand, all Cu(II) halides are known except the iodide. In this case, Cu^{2+} oxidises I^{-} to I_2. However, many copper (1) compounds are unstable in aqueous solution and undergo disproportionation.The stability of Cu^{2+} (aq) rather than Cu^{+}(aq) is due to the much more negative hydration energy than Cu^{+}, which more than compensates for the second ionisation enthalpy of Cu. The ability of oxygen to stabilise the highest oxidation state is demonstrated in the oxides. The highest oxidation number in the oxides coincides with the group number and is attained in $Sc_2O_3$to Mn_2O_7.

	Oxidation number	+7	+6	+5	+4	+3	+2	-1
	3	-	-	-	-	Sc_2O_3	-	-
	4	-	-	-	TiO_2	Ti_20_3	TiO	-
	5	-	-	V_2O_5	V_20_4	V_20_3	VO	-
	6	-	CrO_3	-	CrO_2	Cr_2O_3	CrO	-
Groups	7	Mn_2O_7	-	-	MnO_2	Mn_2O_3,	MnO	-
						Mn_3O_4		
	8	-	-	-	-	Fe_2O_3,	FeO	-
						Fe_3O_4		
	9	-	-	-	-	Co_3O_4	CoO	-
	10	-	-	-	-	-	NiO	-
	11	-	-	-	-	-	CuO	Cu_2O
	12	-	-	-	-	-	ZnO	-

Beyond Group 7, no higher oxides above Fe_2O_3 and Co_3o_4, are known. Although ferrates $Fe(VI)O_4^{2-}$ are formed in alkaline media, they readily decompose to Fe_2O_3 and O_2.

Besides the oxides, oxocations stabilise V(V) as VO^{3+}, V(IV) as VO^{2+} and Ti(IV) as TiO^{2+}. The ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. Thus the highest Mn fluoride is MnF_4 whereas the highest oxide is Mn_2O_7. The ability of oxygen to form multiple bonds to metals explains its superiority. In the covalent oxide Mn_2O_7, each Mn is tetrahedrally surrounded by O's including a Mn-O-Mn bridge. The tetrahedral $[MO_4]_n$ ions are known for V(V), Cr(VI). Mn(V), Mn(Vl) and Mn(VII). Examples of complexes with low oxidation states: $[Ti(CO)_6]^{2-}$(–2), $[V(CO)_6]^{3-}$ (–3), $[Cr(C_6H_6)_{2\backslash}]$ (0), $[Cr(bpy)_3]$ (0), $[Mn(bpy)_3]$ (–1), $[Mn(CO)_5]^-$ (–1), $[Fe(bpy)_3]$ (0), $[Fe(CO)_4]^{2-}$ (–2), $[Co(CO)_4]^-$ (–1), $[Ni(bpy)_2]$ (0), $Ni(CO)_4$ (0), $[Cu(CN)_2]^-$ (+1), $[Cu(CN)_4]^{3-}$ (+1) etc.

4.8 Molecular orbital theory (elementary idea)

The crystal field theory fails to explain many physical properties of the transition metal complexes because it does not consider the interaction between the metal and ligand orbitals. The molecular orbital theory can be very well applied to transition metal complexes to rationalize the covalent as well as the ionic character in metal-ligand bond. A transition metal ion or atom has nine valence atomic orbitals which consist of five nd. three (n+l)p, and one (n+l)s orbitals. These orbitals are of appropriate energy to form bonding interaction with ligands. The molecular orbital theory is highly dependent on the geometry of the complex and can successfully be used for describing octahedral, tetrahedral and square-planar complexes. The main features of molecular orbital theory for metal complexes are as follows:

1. The atomic orbital of metal centre and of surrounding ligands combine to form new orbitals, known as molecular orbitals. Combination is the symmetry permitted overlap between the metal atomic orbitals and suitable ligand group orbitals (LGOs). In the resultant MOs, electrons are placed in terms of their energy as usual.
2. The number of molecular orbitals formed is same as that or number of atomic orbitals combined.
3. The additive overlap results in the bonding molecular orbitals while the subtractive overlap results in the anti-bonding overlap.
4. The energy of bonding molecular orbitals is lower than their nonbonding counterparts while the energy of anti-bonding molecular orbitals is higher than that of non-bonding orbitals.
5. The energy of non-bonding orbitals remains the same.

6. The ionic character of the covalent bond arises from the difference in the energy of combining orbitals.
7. If the energy of a molecular orbital is comparable to an atomic orbital, it will not be very much different in nature from atomic orbital.

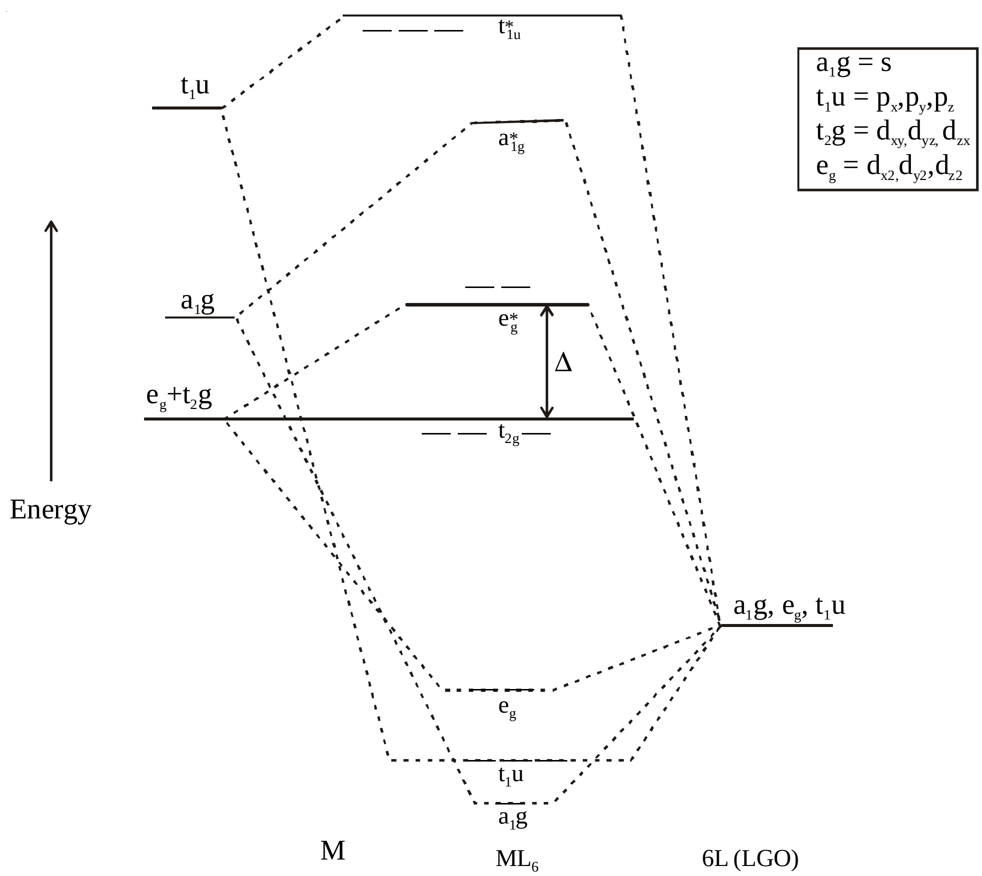
Some typical explanations in the view of MO-theory are:

i) Spin only magnetic moments
ii) 18-electron rule
iii) The splitting of d-orbital
iv) High spin - low spin complexes

4.9 σ and π bonding in octahedral complexes (a pictorial approach)

The σ and π bonding in octahedral complexes is depicted using the following diagrams.

1. σ - bonding in octahedral ML_6 complexes (excluding π-bonds.)



The 6 bonding MO_s (BMO_s) (t_{1u}, eg, a_{1g}) are relatively energetically closer to the ligand orbitals and are attracted more towards the ligands to have polar character. Three metal orbitals of t_{2g} set remain non-bonding. The 6 AB MO's are relatively closer to metal orbitals i.e. they are more enriched with with metal orbital character.

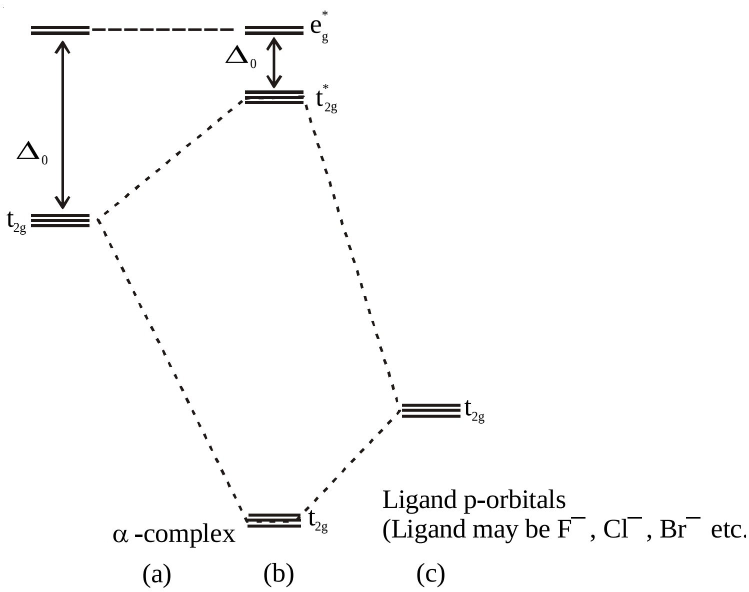
2. π-bonding in octahedral ML_6 complexes

The orbitals on the metal centre which can participate in π-bonding are t_1u and t_2g sets. The t_1u set can also participate in σ-bonding (see for σ-interaction). The σ-bonds being stronger than π-bonds, the metal p orbitals (t_1u set) prefer to form σ-bonds and do not participate in π-bonding interaction. The ligands can provide the following orbitals for π-bonding: (i) pπ-orbitals perpendicular to M-L σ-bond (ii) dπ orbitals (iii) suitable MOs as π^* in polyatonic ligands such as CO, CN^- etc.

The ligands that form π-bonds with metals are generally of two types:

(a) π-donor ligands

(Filled ligand π-orbitals of lower energy than metal t_{2g} orbitals). π-LGOs from 12pπ orbitals of 6 ligands (2 perpendicular π-orbitals per ligand) form $t_{1g} + t_{1u} + t_{2g} + t_{2u}$. LGOs t_{1g}, t_{2u} and t_{1u} remain non-bonding and t_{2g} interacts with metal t_{2g} orbitals (same symmetry). (i.e. t_{2g} orbitals of σ-complex with essentially metal character).



MO diagram for the π-donor interaction (Ligand t_{2g} orbitals lower than σ-complex t_{2g} orbitals).

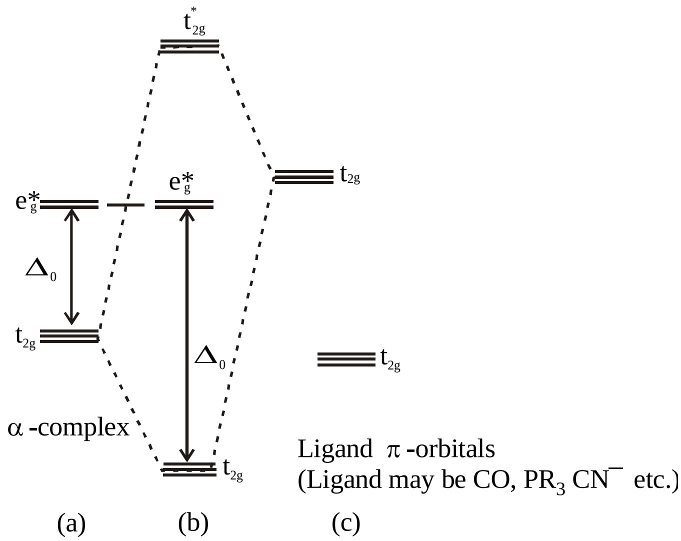
(a) MO's for σ-system of complex (b) MO's after π-interaction

(c) LGO's of t_{2g} symmetry.

(π-t_1u, t_1g, t_2u non-bonding excluded for clarity).

π^*-t_{2g} MO has more metal orbital character while π-t_{2g} (BMO) is enriched with more ligand orbital (LGO) character. The energy difference between σ-eg* and π-t_2g* gives the new Δ_0 value which is smaller compared to that found in absence of π-bonding i.e. only σ-bonding).

b) π - acceptor ligands



MO diagram for the π-axcceptor interaction (Ligand t_{2g} orbitals higher in energy than σ-complex t_{2g} orbitals).

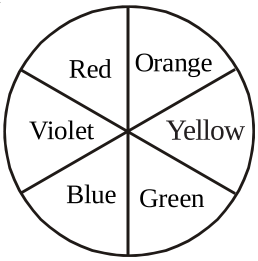
(a) MO's for σ-system of complex (b) MO's after π-interaction

(c) LGO's of t_{2g} symmetry.

π-t_2g LGO's are higher in energy than Ligand σ-complex t_2g orbitals (essentially metal t_2g in σ-complex). The π-t_2g (BMO) has more metal t_2g character and ABMO π^*-t_{2g} becomes enriched with more ligand character. So p-t_{2g} BMO is lower in energy than metal t_{2g} for σ-only bonding and the energy difference between π-t_2g and σ-$_{eg}^*$ gives the new Δ_0 which is greater than the value with no π-bonding.

4.10 Colour and electronic spectra of complexes: selection rules for electronic transitions

The origin of colors in substances can be explained in such a way that when a sample absorbs light, what we see is the sum of the emitted colors that strikes our eyes. It a sample absorbs all wavelength of visible light, none reaches our eyes from that sample, and then the sample appears black. If the sample absorbs no visible light, ft is white or colorless. When the sample absorbs a photon of visible light, it is its complementary color we actually see.



For example, if the sample absorbed orange color, it would appear blue; blue and orange are said to be complementary colors. The visible part of the electromagnetic spectrum contains light of wavelength 380-750 nm. The color wheel above gives information on the wavelength of different color and also the complementary color. For example: if red light is absorbed, the complex appears green; if purple light is absorbed, the complex appears yellow.

Colour of absorbed light	Range in nm	Colour of emitted light
Red	700 to 620	Green
Orange	620 to 580	Blue
Yellow	580 to 560	Violet
Green	560 to 490	Red
Blue	490 to 430	Orange
Violet	430 to 380	Yellow

Selection Rules for Electronic Transitions

The Selection Rules governing transitions between electronic energy levels of transition metal complexes are:

1. The Orbital Rule or Laporte rule $\Delta L = \pm 1$ 2. The Spin Rule $\Delta S = 0$

1. Laporte rule

Statement: Only allowed transitions are those occurring with a change in parity (flip in the sign of one spatial coordinate). In other words, during an electronic transition, the azimuthal quantum number can change only by ± I ($\Delta l = \pm 1$) The Laporte selection rule reflects the fact that for light to interact with a molecule and be absorbed, there should be a change in dipole moment.

The Laporte rule is a spectroscopic selection rule that only applies to centro symmetric molecules (those with an inversion centre) and atoms. It states that electronic transitions that conserve parity, either symmetry or antisymmetry with respect to an inversion centre - i.e., g (gerade = even (German)) $\rightarrow$ g, or u (ungerade = odd) $\rightarrow$ u respectively—are forbidden. Allowed transitions in such molecules must involve a change in parity, either g $\rightarrow$ u or u $\rightarrow$ g. As a consequence, if a molecule is centrosymmetric, transitions within a given set of p or d orbitals (i.e., those that only involve a redistribution ot electrons within a given subshell) are forbidden.

Allowed transitions are those which occur between gerade to ungerade or ungerade to gerade orbitals

Allowed g $\rightarrow$ u & u $\rightarrow$ g

Not allowed (FORBIDDEN) g $\rightarrow$ g & u $\rightarrow$ u

$t_2g \rightarrow e_g$ is forbidden OR d $\rightarrow$ d transitions are not allowed

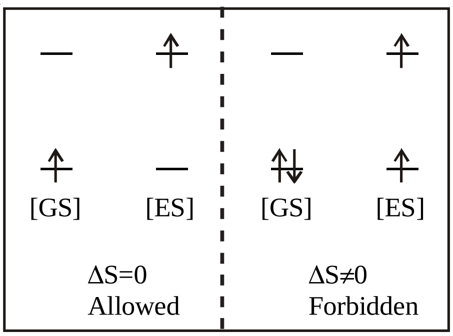
A designation of g for an orbital means there is symmetry with respect to an inversion center. That is, if all the atoms are inverted across the inversion center, the resulting orbital would look exactly the way it did before having inversion applied to it. (This includes same orientation in space). A designation of u means the orbital is antisymmetric with respect to the inversion center, and changes sign everywhere upon inversion. The rule originates from a quantum mechanical selection rule that, during an electron transition, parity should be inverted. However, forbidden transitions are allowed if the centre of symmetry is disrupted, and indeed, such apparently forbidden transitions are then observed in experiments. Disruption of the centre of symmetry occurs for various reasons, such as the Jahn-Teller effect and asymmetric vibrations. Complexes are not perfectly symmetric all the time. Transitions that occur as a result of an asymmetrical vibration of a molecule are called vibronic transitions, such as those caused by vibronic coupling. Through such asymmetric vibrations, transitions that would theoretically be forbidden, such as a d $\rightarrow$ d transition, are weakly allowed.

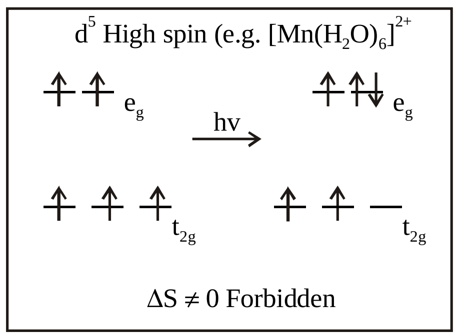
The rule is named after Otto Laporte It is relevant, in particular, ← to ← the electronic spectroscopy of transition metals. Octahedral complexes have a center of symmetry (exact or approximate) so that d → d transitions are forbidden by the Laporte rule and are observed to be quite weak. However tetrahedral complexes have no center of symmetry so that the Laporte rule does not apply, and have more intense spectra.

2. Spin selection rule

Statement: This rule states that transitions that involve a change in spin multiplicity are forbidden. According to this rule, any transition for which $\Delta S = 0$ is allowed and $\Delta S \neq 0$ is forbidden.

During an electronic transition, the electron should not change its spin





Relaxation of the Rates can occur through:

1. Spin-Orbit coupling - this gives rise to weak spin forbidden bands
2. Vibronic coupling - an octahedral complex may have allowed vibrations where the molecule is asymmetric. Absorption of light at that moment is then possible.
3. π-acceptor and π-donor ligands mix with d-orbitals so transitions are not purely d-d.

4.11 Charge transfer transitions (qualitative idea)

A charge-transfer complex (CT complex) or electron-donor-acceptor complex is an association of two or more molecules, or of different parts of one large molecule, in which a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic attraction provides a stabilizing force for the molecular complex. The source molecule from which the charge is transferred is called the electron donor and the receiving species is called the electron acceptor. The nature of the attraction in a charge-transfer complex is not a stable chemical bond, and is thus much weaker than covalent forces. Many such complexes can undergo an electronic transition into an excited electronic state. The excitation energy of this transition occurs very frequently in the visible region of the electromagnetic spectrum, which produces the characteristic intense color for these complexes. These optical absorption bands are often referred to as charge-transfer bands (CT bands). Optical spectroscopy is a powerful technique to characterize charge-transfer bands.

Charge-transfer complexes exist in many types of molecules, inorganic as well as organic, and in solids, liquids and solutions. A well-known example is the complex formed by iodine when combined with starch, which exhibits an intense blue charge-transfer band. Most charge-transler complexes involve electron transfer between metal atoms and ligands. CT bands ot transition metal complexes result from shift of charge density between molecular orbitals (MO) that are predominantly metal in character and those that are predominantly ligand in character. If the transfer occurs from the MO with ligand-like character to the metal-like one. the complex is called a ligand-to-metal charge-transfer (LMCT) complex. If the electronic charge shifts from the MO with metal-like character to the ligand-like one. the complex is called a metal-to-ligand charge-transfer (MLCT) complex. Thus, a MLCT results in oxidation of the metal center, whereas a LMCT results in the reduction of the metal center. Resonance Raman spectroscope is also a powerful technique to assign and characterize CT bands in these complexes.

Energy of charge transfer transitions:

The absorption wavelength of charge-transfer bands, i.e.. the charge-transfer transition energy, is characteristic of the specific type of donor and acceptor entities. The electron donating power of a donor molecule is measured by its ionization potential, which is the energy required to remove an electron from the highest occupied molecular orbital (HOMO). The electron accepting power of the electron acceptor is determined by its electron affinity, which is the energv released when tilling the lowest unoccupied molecular orbital (LUMO). The overall energy balance (ΔE) is the energy gained in a spontaneous charge transfer. It is determined by the difference between the acceptor's electron affinity (E_A) and the donor's ionization potential (E_1), adjusted by the resulting electrostatic attraction (J) between donor and acceptor. $\Delta E = E_A - E_1 + J$

The positioning of the characteristic CT bands in the electromagnetic spectrum is directly related to this energy difference and the balance of resonance contributions of non-bonded and dative states in the resonance equilibrium.

Identification of the charge transfer hands:

1. **Color:** The color of CT complexes is reflective of the relative energy balance resulting from the transfer of electronic charge from donor to acceptor.
2. **Solvatochromism:** In solution, the transition energy and therefore the complex color varies with variation in solvent permittivity, indicating variations in shifts of electron density as a result of the transition. This distinguishes it from the $\pi \rightarrow \pi^*$ transitions on the ligand.
3. **Intensity:** CT absorption bands are intense and often lie in the ultraviolet or visible portion of the spectrum. For inorganic complexes, the typical molar absorptivities, $\in$ arc about 50000 L mol^{-1} cm^{-1}, that are orders of magnitude higher than typical ε of 20 L mol^{-1} cm^{-1} or lower, for d-d transitions (transition from t_2g to e_g). This is because the CT transitions are spin-allowed and Laporte-allowed. However, d-d transitions are potentially spin-allowed but always Laporte-forbidden.

LMCT	MLCT
* e.g. transfer of an electron from p-orbital on a chloride (u symmetry) to a metal's d-orbital (g symmetry) * Favourable when metal centre is in a high oxidation state * Common for π-donor legands (F^-, O^{2-}, N^{3-}, OH^-) * e.g. color of $KMnO_4$ (d^0 complex)	* e.g. transfers of electron from metal's d-orbital to π^* orbital of CO legand. * Favoured electron rich metal centres and those ligated by π-acceptors * Often higher in energy (in the UV region)

Ligand-to-metal (ion) charge transfer: LMCT complexes arise from transfer of electrons from MO with ligand-like character to those with metal-like character. This type of transfer is predominant if complexes have ligands with relatively high-energy lone pairs (example S or Se) or if the metal has low-lying empty orbitals. Many such complexes have metals in high oxidation states (even d^0). These conditions imply that the acceptor level is available and low in energy.

Metal (ion)-to-ligand charge transfer: Metal (ion)-to-ligand charge-transfer (MLCT) complexes arise from transfer of electrons from MO with metal-like character to those with ligand-like character. This is most commonly observed in complexes with ligands having low-lying π* orbitals, especially aromatic ligands. The transition will occur at low energy if the metal ion has a low oxidation number, for its d orbitals will be relatively high in energy.

4.12 L-S coupling and R-S ground state terms for atomic no. 21 to 30

LS-coupling:

When there are unfilled shells in an atom, there may be possibilities to form wave functions that correspond to different electronic states for a given configuration. To get a good understanding of the electronic structure, we must be able to define these states and determine how they are energetically ordered. The answers are found by investigating the non-central contributions to the field and the spin-orbit coupling. The Hamiltonian to be considered is defined by the difference between the full operator and Ho, i.e

$$H' = H - H_0 = \sum_i \left(-\frac{Z}{r_i} - V(r_i) \right) + \sum_{i<j} \frac{1}{r_{ij}} + \sum_i \xi(r_i) I_i s_i$$

We assume that the central contributions to the integral from the first term and substantial parts of the second have been obtained by the SCF (self-consistent field) procedure. Alternatively, we may simply neglect them, since in this connection we are only interested in describing the splitting of a configuration into different electronic states. The interesting part of H' is now rather small and may be treated as a perturbation operator. To proceed systematically, we treat the influence of electron-electron interaction and spin-orbit coupling separately. We start by the former, i.e. consider such atoms where the spin-orbit coupling is considered to be small compared to the electron-electron interaction H_{es} $H_{es} = \sum_{i<j} \frac{1}{r_{ij}}$.

Russell Saunders coupling

The ways in which the angular momenta associated with the orbital and spin motions in many-electron-atoms can be combined together are many and varied. In spite of this seeming complexity, the results are frequently readily determined for simple atom systems and are used to characterize the electronic states of atoms. The interactions that can occur are of three types: A) spin-spin coupling B) orbit-orbit coupling C) spin-orbit coupling

R-S scheme assumes: spin-spin coupling > orbit-orbit coupling > spin-orbit coupling.

This is found to give a good approximation for first row transition series where spin-orbit (J) coupling can generally be ignored. However for elements with atomic number greater than thirty, spin-orbit coupling becomes more significant and the j-j coupling scheme is used.

Spin-Spin coupling: S—the resultant spin quantum number for a system of electrons. The overall spin S arises from adding the individual m_s values together and is a result of coupling of spin quantum numbers for the separate electrons.

Orbit-Orbit coupling: L—the total orbital angular momentum quantum number defines the energy state for a system of electrons. These states or term letters are represented as follows:

Total orbital angular momentum

L	0	1	2	3	4	5
Orbital	S	P	D	F	G	H

Spin-Orbit coupling: Coupling occurs between the resultant spin and orbital momenta of an electron which gives rise to J the total angular momentum quantum number. Multiplicity occurs when several levels are close together and is given by the formula (2S+1).

Terms for $3d^n$ free ion configurations

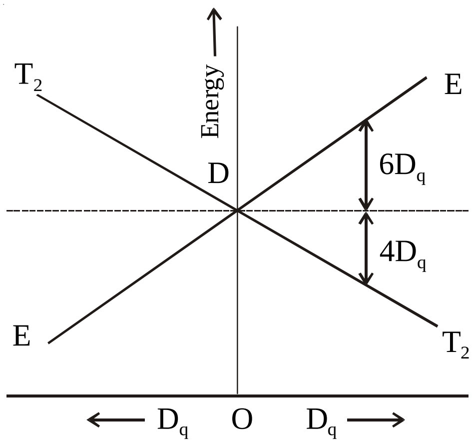
Configuration	Ground state term	Excited state term
d^1, d^9	^2D	-
d^2, d^8	^3F	^3P, ^1G, ^1D. ^1S
d^3, d^7	^4F	^4P, ^2H, ^2G, ^2F, $^2D^1$, ^2D. ^2P
d^4, d^6	^5D	^3H, ^3G, $^2F^1$, ^3F, ^3D, $^3P^1$, ^3P, ^{11}, $^1G^1$, ^1G, ^1F, ^1I, $^1D^1$, ^1D, ^1S, ^1S
d^5	^6S	^4G, ^4F, ^4D, ^4P, ^2I, $^2G^1$, ^2H, ^2G, $^2F^1$, ^2F. $^2D^1$, ^2D. ^2P, ^2S

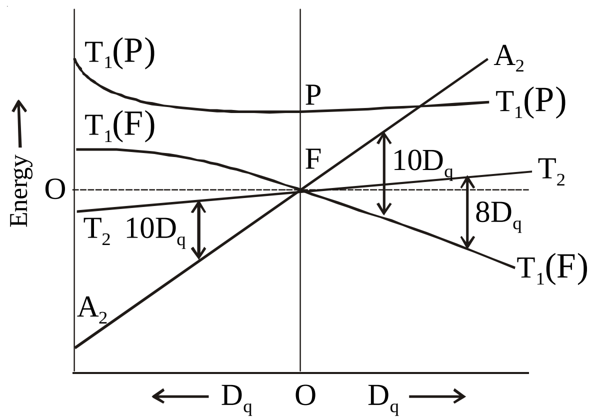
The Russell Saunders term symbol that results from these considerations is given by: (2S+I)L

Configua-ration	Example	Ground state term	m_l 2	1	0	-1	-2	M_L	M_s
d^1	Ti^{3+}	^2D	↑					2	$\frac{1}{2}$
d^2	V^{3+}	^3F	↑	↑				3	1
d^3	Cr^{3+}	^4F	↑	↑	↑			3	$1\frac{1}{2}$
d^4	Cr^{2+}	^5D	↑	↑	↑	↑		2	2
d^5	Mn^{2+}	^6S	↑	↑	↑	↑	↑	0	$2\frac{1}{2}$
d^6	Fe^{2+}	^5D	↑↓	↑	↑	↑	↑	2	2
d^7	Co^{2+}	^4F	↑↓	↑↓	↑	↑	↑	3	$1\frac{1}{2}$
d^8	Ni^{2+}	^3F	↑↓	↑↓	↑↓	↑	↑	3	1
d^9	Cu^{2+}	^2D	↑↓	↑↓	↑↓	↑↓	↑	2	$\frac{1}{2}$

4.13 Qualitative Orgel diagram for $3d^1$ - $3d^9$ ions

Orgel diagrams are correlation diagrams which show the relative energies of electronic terms in transition metal complexes, much like Tanabe-Sugano diagrams. They are named after their creator, Leslie Orgel. Orgel diagrams are restricted to only weak field (i.e. high spin) cases, and offer no information about strong field (low spin) cases. Because Orgel diagrams are qualitative, no energy calculations can be performed from these diagrams; also, Orgel diagrams only show the symmetry states of the highest spin multiplicity instead of all possible terms, unlike a Tanabe-Sugano diagram. Orgel diagrams will, however, show the number of spin allowed transitions, along with their respective symmetry designations. In an Orgel diagram, the parent term (P. D, or F) in the presence of no ligand field is located in the center of the diagram, with the terms due to that electronic configuration in a ligand field at each side. There are two Orgel diagrams, one for d^1, d^4, d^6 and d^9 and the other with d^2, d^3, d^7 and d^8 configurations.





d^1,d^6(tetrahedron) d^1,d^6 (octahedron) d^2,d^7 (tetrahedron) d^2,d^7 (Octahedron)

d^4,d^9(octahedron) d^4,d^9(tetrahedron) d^3,d^8(octahedron) d^3,d^8(tetrahedron)

The inverse relationship between the two symmetries (Oct and tet) arises because a tetrahedral field is in effect, a negative actahedral field. For the second diagram, the effect of mixing of terms is represented. As a general rule, terms having identical symmetry will mix, with the extent of mixing being inversely propertional to the energy difference between them. For d^7 the terms involved are the two T_1 (tet) and T_1g (Oct.) levels. The upper level is raised in energy while the lower level falls. This is represented in the diagram as diverging lines for the pairs of T_1g and T_1 levels. The terms include 'g' in oct.field, but not in tet.field. For example for the first diagram on the left hand side, the d^1,d^6 (tet) have the terms E and T^2, but for d^4,d^9 (oct.) the terms are Eg and T_{2g}.

4.14 Summary

Coordination compounds is the study of complexes of transition metals and different interactions of these complexes under different conditions. In this chapter the structure and bonding of coordination compounds on the basis of valence bond theory along with its limitations are discussed briefly. Valence bond theory does not differentiate between the strong and weak ligands and hence the same is explained later by Crystal Field Theory. It is mainly based on the splitting of metal d orbitals in presence of ligands. The Jahn Teller theorem and its applications are also discussed accordingly. The limitations of Crystal Field Theory along with nephalauxetic effect are also discussed in detail. The different aspects for stabilization of unusually high and low oxidation states of 3d series elements is discussed. Elementary idea about molecular orbital theory is given. Transition metals are responsible for colours in substances. This is being explained using the Newtons colour disc. The CT, L-S and R-S ground state term symbols are discussed along with Orgel diagrams. Their explanation and diagrams are also provided in this chapter.

4.15 Self Assessment Questions

1. State Valence bond theory.
2. Predict the hybridisation, shape and nature of - $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$. $[NiCl_4]^{2-}$, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$.
3. State the limitations of Valence bond theory.
4. State crystal field theory.
5. Write the factors affecting crystal field theory.
6. Show crystal field splitting in octahedral and tetrahedral fields.
7. What do you mean by Jahn Teller diatortion?
8. State the limitations of crystal field theory.
9. What is nephelauxetic effect?
10. Write the main features of MOT.
11. Why do transition metals and their complexes show colours?
12. State the Selection Rules for Electronic Transitions.
13. Write the statement of Laporte rule.
14. Write the statement for spin selection rule.
15. What do you mean by charge transfer spectra?
16. How can the CT bands be identified?
17. Write the differences between LMCT and MLCT.
18. What do you mean by R-S coupling?
19. What do you mena by Orgel diagrams?
20. Draw the Orgel diagrams for d^1. d^4, d^6, and d^4 configurations.

21. Draw the Orgel diagrams for d^2, d^3, d^7, and d^8 configurations.

Answer

1. See section 4.1	2. See section 4.1	3. See section 4.1
4. See section 4.2	5. See section 4.2	6. See section 4.2
7. See section 4.3	8. See section 4.4	9. See section 4.5
10. See section 4.7	11. See section 4.9	12. See section 4.9
13. See section 4.6	14. See section 4.9	15. See section 4.10
16. See section 4.10	17. See section 4.10	18. See section 4.11
19. See section 4.12	20. See section 4.12	21. See section 4.12

4.16 Further Reading

1. Essential Trend in Inorganic Chemistry, Mingos, Oxford University Press, 2004
2. Basic Inorganic Chemistry, Cotton, Wilkinson, Gans 3rd Ed. John Wiley Sons, Inc., 2004.
3. Fundamental Concepts of Inorganic Chemistry, A. K. Das and M. Das, Volume-2, First Ed., 2015.

Unit 5 ❑ Reaction Kinetics and Mechanism

5.0 Objectives

After reading this unit you can be able to know the following factors—

* Definition of substitution reaction and its application in square planar complexes.
* Trans effect theories and applications.
* Elementary concept of Cis-effect.

5.1 Introduction to Inorganic reaction mechanisms

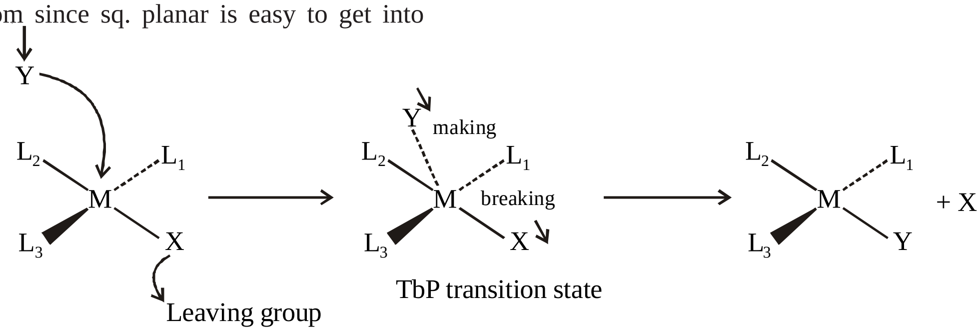
Transition metal Ions and complexes play a fundamental role in at least three areas of research: (i) bioinorganic chemistry and molecular biology, in investigating the functions of metal complex metalloproteins (ii) industrial chemistry, in exploiting metal complexes as homogeneous catalysts for the optimization of very important commercial processes, such as polymerization, hydroformylation, hydrogenation, oxidation of olefins, etc. (iii) environmental and medicinal chemistry. Understanding the mechanism of the reactions at transition metal sites is then crucial in designing new inorganic materials, developing industrial homogeneous catalysts and gaining insight into the role of metalloenzymes in biological processes and metals in medicine. The old motto "every little reaction has a mechanism all its own" appears to be incorrect because, at the present time, the mechanistic tools developed for the analysis of kinetic and extra kinetic data have proved their worth in the classification of a wide range of reaction types in coordination, organometallic and bioinorganic chemistry. A mechanism is then a predictive theoretical construction that must account for all the kinetic, spectroscopic and theoretical information currently available on a reaction. The mechanistic picture is always on trial and it can or cannot survive to future results coming from the use of rnore sophisticated experimental and theoretical techniques. In this chapter a description is reported of some fundamental reactions in transition metal ch'emistry that have established the pattern of reactivity on which contemporary studies are based.

Monitoring the rate of a reaction occurring in solution usually requires the measure of a physical property of the system directly related to the concentration changes of reactant or products by the use of simple or of sophisticated methods. Any measurement that gives the amount ot material as a function of time can be used to generate kinetic data. A variety of spectroscopic techniques are appropriate to the purpose such as ultraviolet/visible (UV/VIS) or infrared (1R) spectroscopy, fluorescence, circular dichroism (CD), nuclear magnetic resonance (NMR), etc. and the choice will depend upon the type of reaction and the rate of reaction.

5.2 Substitution reactions in square planar complexes

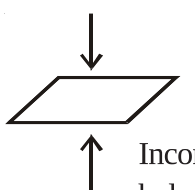
Square planar is the common geometry for the d^8 metal ions. Much of the discussion in this section deals with Pt(II) square-planar complexes. For square planar both bond-breaking and bond making are important in the reaction mechanism and the mechanism is an associative mechanism.

entering group can approach from top or bottom since sq. planar is easy to get into



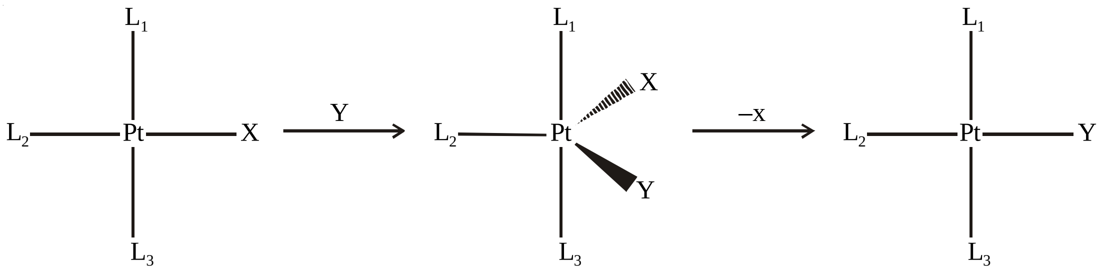
Stereospecific - X (leaving group) is trans to L_2 and so is Y (entering group)

Incoming ligand attacks from above the square plane

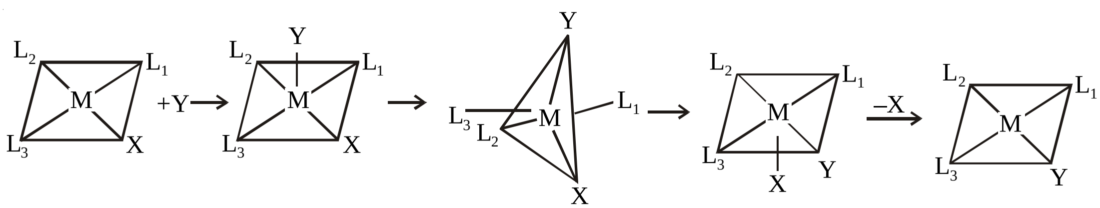


Plane containing Pt(II) and four iiaands.

Incoming ligand attacks from below the square plane



Initial attack by the entering group at a square planar Pt(lI) centre is from above or below the plane. Nucleophile Y then coordinates to give a trigonal bipyramidal intermediate species which loses X with retention of stereochemistry. The incoming ligand approaches a vacant axial site of the square planar complex to form a square pyramidal intermediate (or transition state).



Intramolecular rearrangement via a trigonal bipyramid generates a different square pyramidal structure with the incoming ligand now in the basal plane. (This motion is closely related to the Berry psludorotation). The reaction is completed by the leaving group departing from an axial site. Note that the stereochemistry of the complex is retained during the substitution process. Therefore the substitution in square planar complexes generally proceeds by bionolecular displacement (S_N2) mechanism.

Examples: $ML_2X_2L^1 \xrightarrow{\text{Solvent}} MLL^1X + L$

Factors affecting rate of Substitution:

1. Role of the Entering Group

The rate of substitution is proportional to the nucleophilicity of entering group, i.e. for most reactions of Pt(ll), the rate constant increases in the order:

$$H_2O < NH_3 = py < Br^- < I^- < CN^-.$$

The ordering is consistent with Pt(ll) being a soft metal centre.

2. The Role of The Leaving Group

For the reaction $[Pt(dien)X]^+ + py \longrightarrow [Pt(dien)(py)]^+ + X^-$

In H_2O at 25°C the sequence of lability of X^- (leaving group) is :

$$H_2O > Cl^- > Br^- > I^- > N_3^- > SCN^- > NO_2^- > CN^-$$

with a spread of over 10^6 in rate across series. The leaving group does not affect the nucleophiles discrimination factors, only the intrinsic reactivity. The series tend to parallel the strength of the Metal-ligand bond.

3. The Nature of the Other Ligands in the Complex

Trans effect (discussed later)

4. Effect of the Metal Centre

The order of reactivity of a series of isovalent ions is: Ni(Il) > Pd(11) >> Pt(ll). This order of reactivity is the same order as the tendency to form 5-coordinate complexes. More is it easier for the formation of a 5-coordinate intermediate complex, greater is the stabilization of the transition state and so the greater the bimolecular rate enhancement.

5.3 Trans effect - theories and applications

The trans effect is best defined as the effect of a coordinated ligand upon the rate of substitution of ligands opposite to it or the ability of a ligand in a square planar complex to direct the replacement of the ligand trans to it.

By measuring rates a series of ligande can be put into an order of decreasing trans-effect. The approximate order of decreasing trans-effect of some common ligands is:

The trans effect is given as the following series:

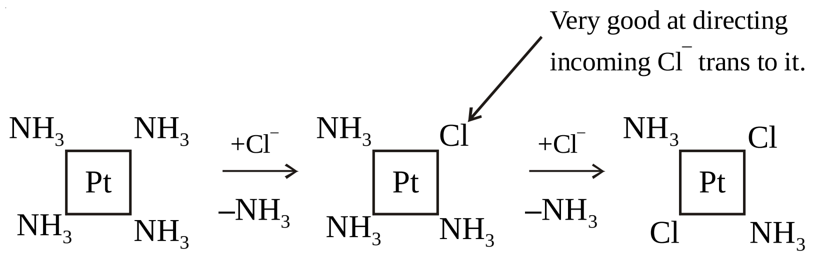
$$CN^- > NO_2^- > I^- = SCN^- > Br^- > CI^- > py > NH_3 > H_2O$$

The Trans Effect in Practice

1. $[Pt(NH_3)_4]^{2+} \xrightarrow{2Cl^-} trans\text{–}[Pt(NH_3)_2Cl_2]$
2. $[Pt(CI)_4]^{2-} \xrightarrow{2NH_3} cis\text{–}[Pt(NH_3)_2Cl_2]$

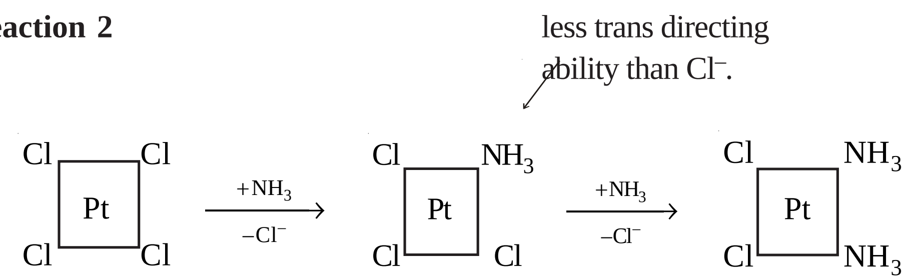
} why the different isomers?

Reaction 1



$[Pt(NH_3)_4]^{2+}$ $[Pt(NH_3)_3Cl]^{+}$ trans-$[Pt(NH_3)_2Cl_2]$

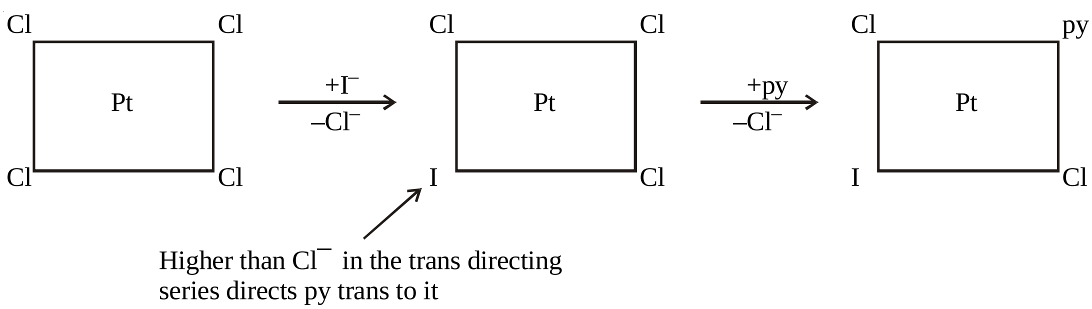
Reaction 2



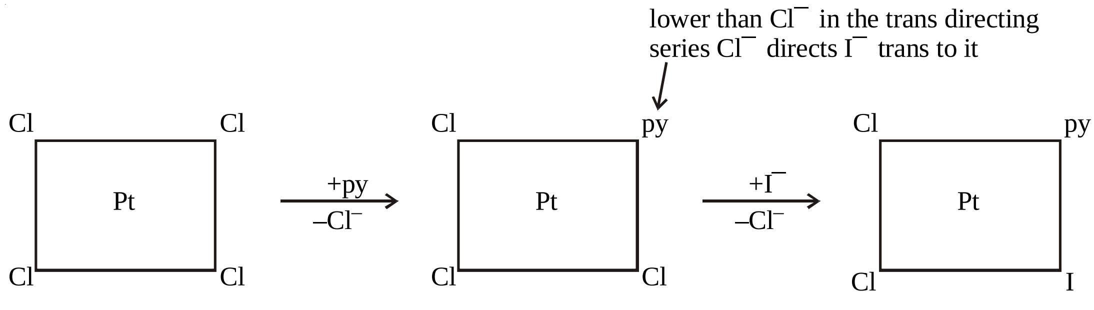
$[PtCl_4]^{2-}$ $[Pt(NH_3)Cl_3]^{-}$ cis-$[Pt(NH_3)_2Cl_2]$

Feature's:

- Cl^- has a greater trans directing effect than NH_3.
- Trans directing series $Cl^- > NH_3$
- Depends on order in which the reagents are added as to which geometric isomer is formed so has uses for devising synthesis of Pt(Il) complexes. E.g. consider the preparation of cis and trans $PtCl_2I(py)^-$ from $PtCl_4^{2-}$, I^- and py.

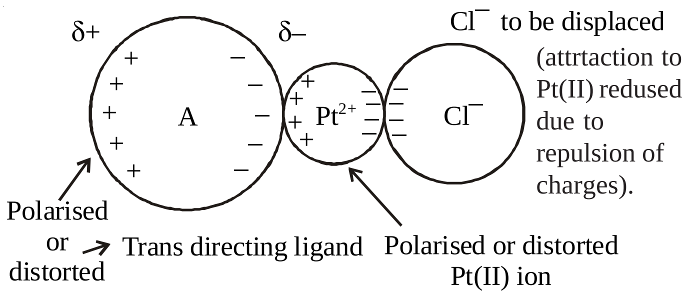


$[PtCl_4]^{2-}$ $[PtCl_3I]^{2-}$ Trans-$[PtCl_2I(py)]^-$

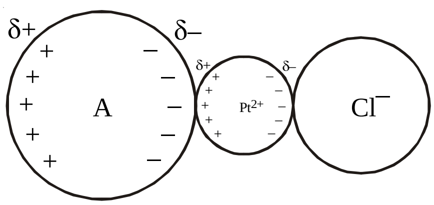


$[PtCl_4]^{2-}$ $[PtCl_3(py)]^-$ Cis-$[PtCl_2I(py)]^-$

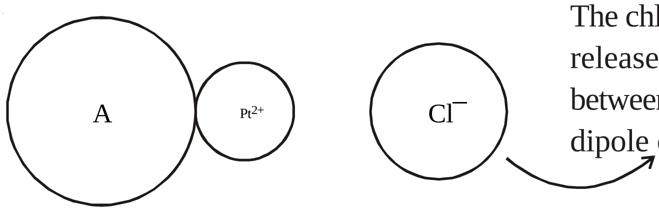
Polarization Theory:



The Pt(II) cation induces a dipole in the polorizable trans-directing ligand A.



The induced dipole in ligand A indues a dipole in the polarizable Pt(II) cation.

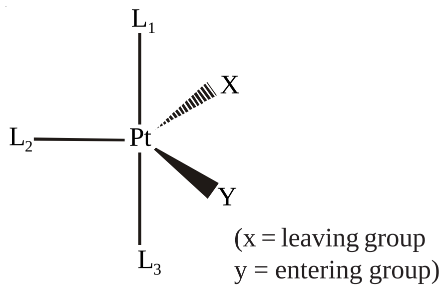


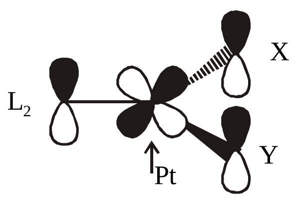
The chloride anion trans to A is more easily released due to the extra repulsive forces between its negative charge and the induced dipole of the Pt(II) cotion.

Support for this theory is demonstrated by looking at the trans directing series. The more polarizable ligands such as SCN^-, and I^- and the ligands containing π-clouds e.g. CN^- are high in the series, whereas less polarizable ligands such as ammonia or water are lower in the series. Additional support comes from the observation that Pt(ll) complexes demonstrate a more pronounced trans effect than those of the less polarizable Pd(ll) and Ni(II) cations.

Other contributing factors to the trans-effect:

In the trigonal plane of the 5-coordinate transition state or intermediate, a π- bonding interaction can occur between a metal d-orbital (e.g. d_{xy}) and suitable orbitals (p atomic orbitals, or molecular orbitals of p-symmetry) of ligand L_2 (the ligand trans to the leaving group) and Y (the entering group). These 3 ligands and the metal centre can communicate electronically through π-bonding only if they all lie in the same plane in the transition state or intermediate. This implies the 5-coordinate species must be trigonal pyramidal.





trigonal bipyramidal transition state or intermediate

π-bonding in the trigonal plane

Rules:

1. It is easier to replace Cl^- than most other ligands.
2. To displace some other ligands with Cl^-, a huge excess of Cl^- must be added.
3. If there is more than one possibility for replacing the $C1^-$, the one that is replaced is the one trans to the ligand higher in the series.
4. Part of the general order for the trans effect (the ability of ligands to direct trans-substitution) is :

$$CN^- > NO_2^- > I^- > SCN^- > Br^- > Cl^- > py > NH_3 > H_2O$$

5. A strong π-acceptor e.g. CN^- will stabilize the transition state by accepting electron density that the incoming nucleophile donates to the metal centre, and will thereby facilitate substitution at the site trans to it. The vacant π or π* orbital of π-bonding ligands accept a pair of electrons from filled d-orbitals of the metal to form metal ligand π-bond (either dπ-pπ or dπ-dπ). The formation of π-bond in the complex increases the electron density in the direction of L_2 and diminishes it in the direction of X trans to L_2. So Pt–X bond weakens.

5.4 Lability and inertness in octahedral complexes towards substitution reactions

The concept of lability and inertness was first explained by Henry Taube (Nobel Prize, 1983). He tried to understand lability by comparing the factors that govern bond strengths in ionic complexes to observations about the rates of reaction of coordination complexes. He saw some things that were surprising. Taube observed that many M^{+1} ions (M = metal) are more labile than many M^{3+} ions, in general. That is not too surprising, since metal ions function as Lewis acids and ligands function as Lewis bases in forming coordination complexes. In other words, metals with higher charges ought to be stronger Lewis acids, and so they should bind ligands more tightly. However, there were exceptions to that general rule. For example, Taube also observed that Mo(V) compounds are more labile than Mo(III) compounds. That means there is more going on here than just charge effects. Another factor that governs ionic bond strengths is the size of the ion. Typically, ions with smaller ionic radii form stronger bonds than ions with larger radii. Taube observed that Al^{3+}, V^{3+}, Fe^{3-} and Ga^{3+} ions are all about the same size. All these ions exchange ligands at about the same rate.

The transformation of one complex into other is determined by thermodynamic stability when the system has reached equilibrium while kinetic stability refers to the speeds at which these take place. The stability depends upon the difference in energy of the reactant and product. If the product has less energy than that of reactant, it will be more stable as compared to reactant. Thermodynamic stability of metal complexes is calculated by the overall formation constant (stability constant).

The kinetic stability of the complex depends upon the activation energy of the reaction, If the activation energy barrier is low, reaction will take place at higher speed. These types of complexes are also called kinetically unstable or labile. If the activation energy barrier is high, the substance will react slowly and will be called as kinetically stabilized or inert. There is no correlation between thermodynamic and kinetic stability. Thermodynamically stable product may labile or inert and the vice versa is also true.

In accordance to valence bond theory, octahedral metal-complexes can be divided into two types.

A. Outer orbital complexes: Complexes with sp^3d^2 hybridization are generally) labile in nature. Valence bond theory proposed that the bonds in this hybridization are generally weaker than d^2sp^3 and therefore they show labile character.

B. Inner orbital complexes: Since d^2sp^3 hybrid orbitals have six electron pairs donated by the ligands, hence these hybrid orbitals can form both inert and labile complexes.

In terms of CFT any increase in the crystal field stabilization energy will make a complex labile while the decrease in CFSE will make complex inert. The calculation of CFSE is done by using the following:

1. Complexes with coordination number six should be treated as perfect octahedral even if mixed ligands are present.
2. Inter-electronic repulsive forces should be neglected
3. Δ_o -Magnitude for reacting as well as the intermediate complexes are assumed to be same though they might have considerably different values.
4. JahnTeller distortion is to be neglected in all evidences for the lability and inertness.

Table I. CFSE values of high-spin (HS) and low-spin (LS) octahedral complexes undergoing ligand displacement reactions through SN_1 mechanism (Dissociation Mechanism)

$MX_5Y+Z \rightarrow MX_5Z + Y$ (Intermediate is 5-coordinate of sq. py. or tbp geometry).

Configuration	CFSE for octahedral (Coordination No - 6) (Dq)	CFSE for square pyramidal intermediate (Coordination No - 5) (Dq)	Gain or loss of CFSE Negative=gain Positive=loss (Dq)	Kinetic stability
d^0	0	0	0	Labile
d^1	–4	–4.57	–0.57	Labile
d^2	–8	9.14	–1.14	Labile
d^3	–12	10	+2.00	Inert
d^4 (HS)	–6	–9.14	–3.14	Labile
d^4 (LS)	–16	–14.57	+1.4.3	Inert
d^5 (HS)	0	0	0	Labile

Configuration	CFSE for octahedral (Coordination No - 6) (Dq)	CFSE for square pyramidal intermediate (Coordination No - 5) (Dq)	Gain or loss of CFSE Negative=gain Positive=loss (Dq)	Kinetic stability
d^5 (LS)	–20	–19.4	+0.86	Inert
d^6 (HS)	–4.00	–4.57	–0.57	Labile
d^6 (LS)	–24	–20	+4.00	Inert
d^7 (HS)	–8	–9.14	–1.14	Labile
d^7 (LS)	–18	–19.14	–1.14	Labile
d^8	–12	–10	+2.00	Inert
d^9	–6	–9.14	–3.14	Labile
d^{10}	0	0	0	Labile

Table 2. CFSE values of high-spin (HS) and low spin (LS) octahedral complexes undergoing ligand displacement reactions through S_n2 mechanism (Associative Mechanism)

$MX_5Y+Z \rightarrow MX_5YZ \rightarrow MX_5Z+Y$ (Intermediate is 7-coordinate).

Configuration	CFSE for octahedral reactant (Coordination No - 6) (Dq)	CFSE for octahedral-wedge intermediate (Coordination No - 7) (Dq)	Gain or loss of CFSE Negative=gain Positive=loss (Dq)	Kinetic stability
d^0	0	0	0	Labile
d^1	4	6.08	-2.08	Labile
d^2	-8	-8.68	-0.68	Labile
d^3	-12	-10.20	+1.80	Inert
d^4 (HS)	-6	-8.79	-2.79	Labile
d^4(LS)	-16	-16.26	-0.26	Labile

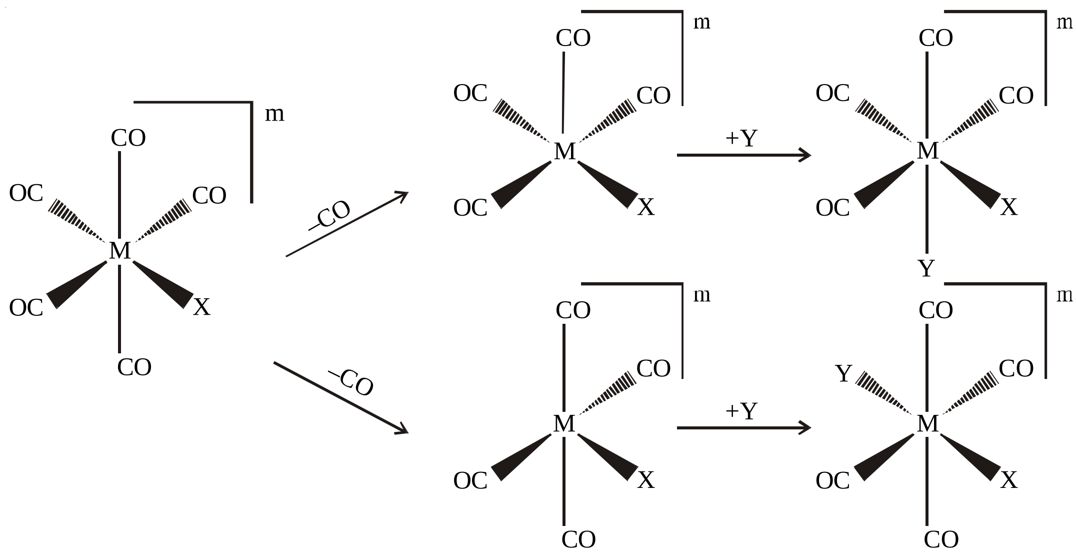
Configuration	CFSE for octahedral reactant (Coordination No - 6) (Dq)	CFSE for octahedral-wedge intermediate (Coordination No - 7) (Dq)	Gain or loss of CFSE Negative=gain Positive=loss (Dq)	Kinetic stability
d^5 (HS)	0	0	0	Labile
d^5 (LS)	–20	–18.86	+1.14	Inert
d^6 (HS)	–4	–6.08	–2.08	Labile
d^6 (LS)	–24	–20.37	+3.63	Inert
d^7 (HS)	–8	–8.68	–0.68	Labile
d^7 (LS)	–18	–18.98	–0.98	Labile
d^8	–12	–10.20	+1.80	Inert
d^9	–6	–8.79	–2.79	Labile
d^{10}	0	0	0	Labile

Factors affecting kinetic stability and lability of non-transition metal complexes:

1. Charge on the central metal ion.
2. Radii of the central metal ion.
3. Ratio of charge to ionic size
4. Molecular geometry of the complex

5.5 Elementary concept of cis-effect

Cis effect is defined as the labilization (making unstable) of CO ligands that are cis to other ligands. CO is a well-known strong pi-accepting ligand in organometallic chemistry that will labilize in the cis position when adjacent to ligands due to steric and electronic effects. The system most often studied for the cis effect is an octahedral complex $M(CO)_5X$ where X is the ligand that will labilize a CO ligand cis to it. Unlike trans effect, where this property is most often observed in 4-coordinate square planar complexes, the cis effect is observed in 6-coordinate octahedral transition metal complexes. It has been determined that ligands that are weak sigma donors and non-pi acceptors seem to have the strongest cis-labilizing effects. Therefore, the cis effect has the opposite trend of the trans-effect, which effectively labilizes ligands that are trans to strong pi accepting and sigma donating ligands.



Group 6 and group 7 transition metal complexes [$M(CO)_5X$] have been found to be the most prominent with regard to dissociation of the CO cis to ligand X. CO is a neutral ligand that donates 2 electrons to the complex, and therefore lacks anionic or cationic properties that would affect the electron count of the complex. For transition metal complexes that have the formula $M(CO)_5X$, group 6 metals (M^o,where the oxidation state of the metal is zero) paired with neutral ligand X, and group 7 metals (M^+, where the oxidation state of the metal is +1), paired anionic ligands, will create very stable 18 electron complexes. Transition metal complexes have 9 valence orbitals, and 18 electrons will in turn fill these valence shells, creating a very stable complex, which satisfies the 18-electron rule. The cis-labilization of 18 e- complexes suggests that dissociation of ligand X in the cis position creates a square pyramidal transition state, which lowers the energy of the $M(C0)_4X$ complex, enhancing the rate of reaction. The scheme shows the dissociation pathway of a CO ligand in the cis and trans position to X, followed by the association of ligand Y. This is an example of a dissociative mechanism, where an 18 e- complex loses a CO ligand, making a 16 e- intermediate, and a final complex of 18 e- results from an incoming ligand inserting in place of the CO. This mechanism resembles the SN^1 mechanism in organic chemistry, and applies to coordination compounds as well.

The order of ligands which possess cis-IabiIizing effects are as follows:

$$CO, AuPPh_3, H^-, SnPh_3, GePh_3, M(CO)n < P(O)Ph_3 < PPh_3 < I^- < CH_3SO^{2-}.$$
$$NC_5H_5 < CH_3CO < Br^-, NCO^- < CI^- < NO_3^-$$

Anionic ligands such as F^-, Cl^-, OH^-, and SH^- have particularly strong CO labilizing effects in $[M(CO)_5L]^-$ complexes. This is because these ligands will stabilize the 16 e– intermediate by electron donation from the p-pi lone pair donor orbital. Other sulfur-containing ligands, particularly thiobenzoate, are other examples of particularly useful CO cis-labilizing ligands, which can be explained by stabilization of the intermediate that results upon CO dissociation. This can be attributed to the partial interaction of the oxygen from the thiobenzoate and the metal, which can eliminate solvent effects that can occur during ligand dissociation in transition metal complexes.

5.6 Summary

Chemical kinetics, also known as reaction kinetics, is the branch of physical chemistry that is concerned with understanding the rates of chemical reactions. It is to be contrasted with thermodynamics, which deals with the direction in which a process occurs but in itself tells nothing about its rate. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that also can describe the characteristics of a chemical reaction. The inorganic reaction mechanism and kinetics involve detailed studies about the cis and trans effects. The details of substitution reactions involved associative and dissociative mechanisms. The lability and inertness of octahedral complexes have also been discussed in this chapter.

5.7 Self Assessment Questions

1. What do you mean by inorganic reaction mechanism?
2. Explain the mechanism of substitution reactions in square planar complexes.
3. State the factors affecting rate of substitution reactions.
4. What is trans effect?
5. Mention the features of trans effect.
6. Explain lability and inertness of octahedral complexes towards substitution reactions.
7. What do you mean by cis effect?

Answer Key

1. See section 5.1 2. Sec section 5.2 3. See section 5.2

4. See section 5.3 5. See section 5.3 6. See section 5.4

7. See section 5.5

5.8 Further Reading

1. Comprehensive Coordination Chemistry, S.P. Banerjee, Books & Allied Publication.

2. Fundamental Concepts of Inorganic Chemistry, A.K. Das and M. Das, Volume-2, First Ed., 2015

3. Essential Trend in Inorganic Chemistry, Mingos, Oxford University Press (Ind. Ed.) 2004.

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