

Spin magnetic moment calculations-

$$\mu_s = \sqrt{4s(s+1)}$$

μ_s = Spin magnetic moment

s = Sum of spin quantum number of e's ($s = \frac{1}{2}$)

e.g. for one unpaired electron.

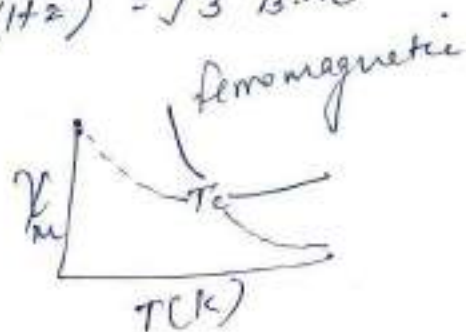
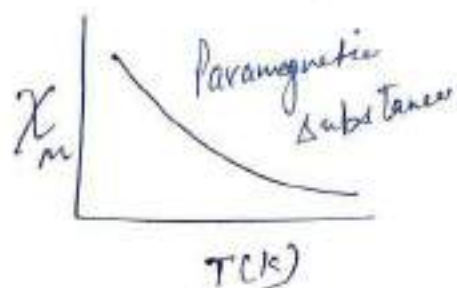
$$s = \frac{1}{2}$$

$$\mu_s = \sqrt{4 \times \frac{1}{2} \left(\frac{1}{2} + 1\right)} = \sqrt{3} \text{ B.M.}$$

= μ_s also calculated as,

$$\mu_s = \sqrt{n(n+2)} \text{ B.M.}$$

e.g. 1 electron = $\sqrt{1(1+2)} = \sqrt{3} \text{ B.M.}$



Above Curie temperature ferromagnetic substances behave paramagnetic

Crystal Field Stabilization Energies (CFSE) or Δ_0

The change in energy of d-orbitals under the influence of electric field of ligands is known as CFSE or Δ_0 .

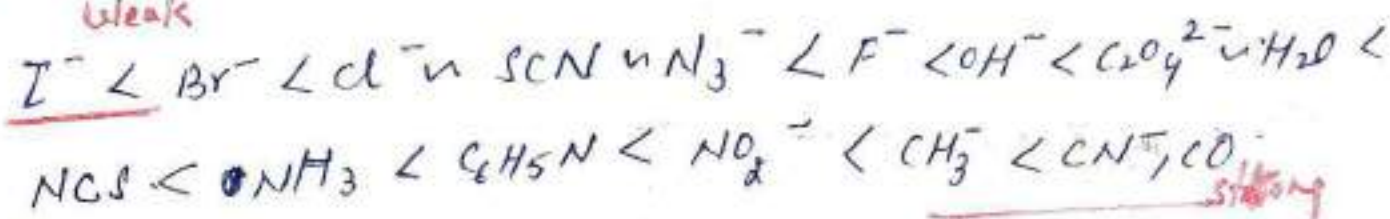
It is equal to $\Delta_0 = 10Dq$

change in energy in terms of $Dq = [0.4x + 0.6y] \times 10Dq$
 $= [-4x + 6y] Dq$

For octahedral complexes.

* Spectrochemical Series

Weak

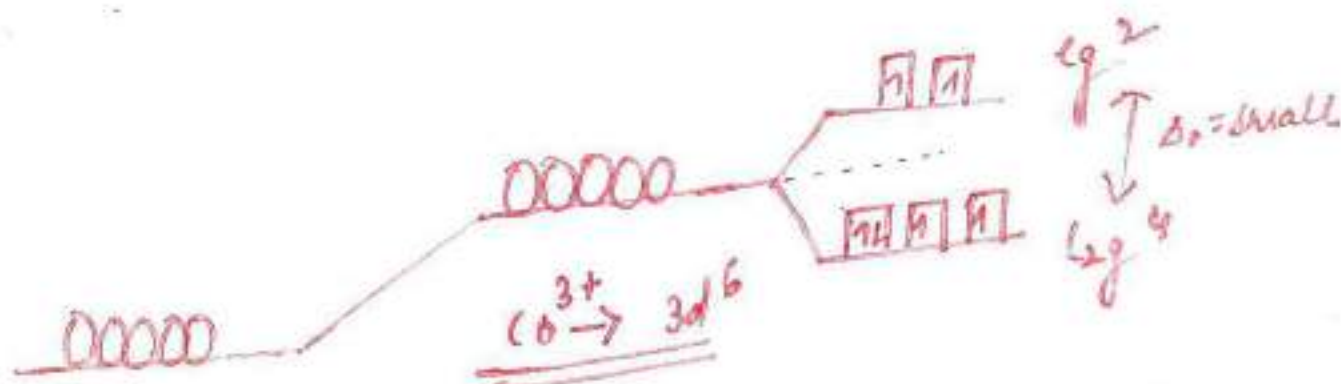


Strong

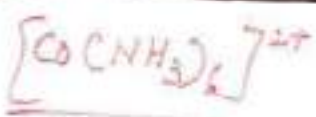
weak field ligand

Strong field ligands

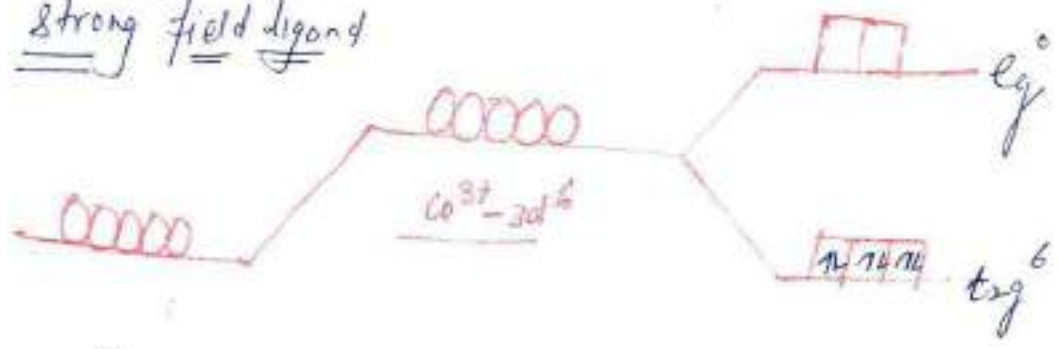
Fig: Formation of $[CoF_6]^{3-}$ which contains weaker ligands



$$(-4 \times 4 + 6 \times 2) = -16 + 12 = -4 Dq$$



strong field ligand



$$\Delta_0 = \{4 \times 6 + 6 \times 0\} Dq = -24 + 0 = -18 Dq$$

and Theory of Solids p¹

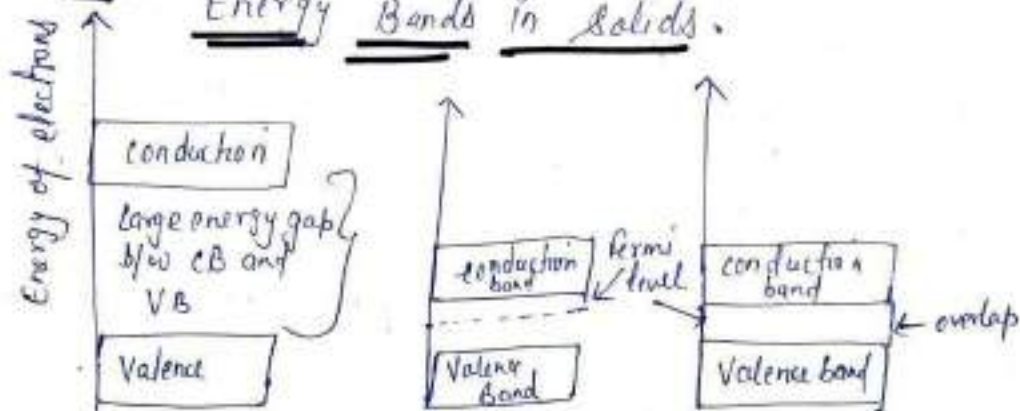
Dr. M. S. 9

In 1927 Walter Heitler and Fritz London discovered bond - very closely spaced orbitals with not so much difference in energy.

With the help of band Theory we can easily explain why some solids are good conductor of electricity (metals) and others are non-conductors or insulators (non-metals) or semi-conductors (semi-metals).

Fig:

Energy Bands in Solids.



(a) Insulator

(b) Semiconductor

(c) Conductor

Molecular orbital theory extended to solids is also known as Band Theory. Energy of electrons in each subshell is definite. These definite energy values are called energy levels of the atoms.

Classification of Solids \rightarrow on the basis of the structure of solids, these can be classified into three different groups.

- (1) Metals
- (2) Insulators
- (3) Semiconductors.

Metal \rightarrow The conduction in metals is only due to the electrons. In this case there is no forbidden energy gap between the valence and conduction bands. The two bands actually overlap with each other (Fig 1.9). The valence band energies are the same as the conduction band energies in the metals. It is very easy for a valence electron to become a free electron. Therefore without supplying any additional energy such as heat or light, a metal already contains a large number of free electrons and that is why it works as a good conductor.

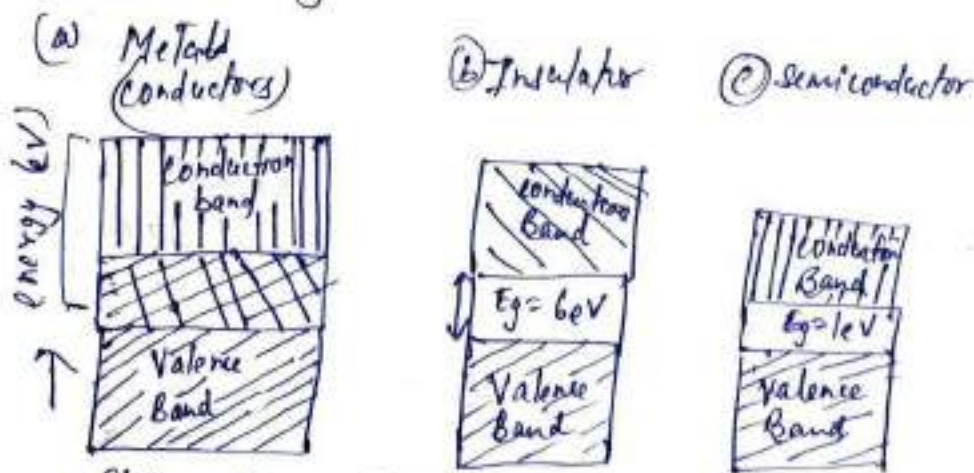


Fig. - Energy Band Diagram

Insulator: \rightarrow An insulator is a material having extremely poor electrical conductivity. In this case the valence band is completely filled and conduction band is completely empty. It has a very wide forbidden energy gap e.g. for diamond it is 6eV. Therefore, a very large amount of energy is required for the electrons to move from valence band to conduction band.

Because of this, it is practically impossible for an electron in the valence band to jump to the conduction band. The conduction band, therefore, continues to remain almost empty. Thus, no current flows through such a solid and it behaves as an insulator.

Semiconductor \rightarrow The semiconductor has conductivity much greater than that of an insulator but much smaller than that of a metal. The forbidden energy gap in this case is of the order of 1eV. at ^{absolute} zero temp the V.B is completely filled and C.B is totally empty. Hence they are ~~not~~ ~~not~~ insulators at low temp. However, at room temperature, the thermal energy is sufficient to lift the e's from V.B to conduction band.

* Resistance of semiconductor decreases with the rise in temp

Role of Doping on Band structure \Rightarrow

Doping: \Rightarrow The process of addition of impurity to a semi-conductor so as to increase its conductivity is called as doping.

Dopant \Rightarrow The impurity atoms are called as dopants.

Doped or ~~extrinsic~~ Extrinsic Semiconductor: \Rightarrow The semiconductor containing the impurity atoms are called as doped or extrinsic semiconductor.

The amount of impurity added in semiconductor is very small say 1 in 10^6 to 10^8 atoms, so there is no structural change in the semiconductor but the conductivity of the material is greatly affected by this doping.

Intrinsic Semiconductors \Rightarrow An intrinsic semiconductor, also called an undoped semiconductor or i-type semiconductor.

Types of Semiconductors: \Rightarrow Depending upon the impurity added the extrinsic semiconductors are classified.

- (1) N-Type semiconductor.
- (2) P-type semiconductor.

Donor or N-type Semiconductors \Rightarrow

When a pentavalent impurity atom of group (V) is introduced into the semiconductor, the resulting extrinsic semiconductor is called N-type semiconductor.

Let us consider that an impurity of phosphorous is added to Si. four of its five valence electrons form covalent bond with the neighbouring four Si-atoms while the fifth valence electron remains loosely bound to its nucleus as shown in figure.

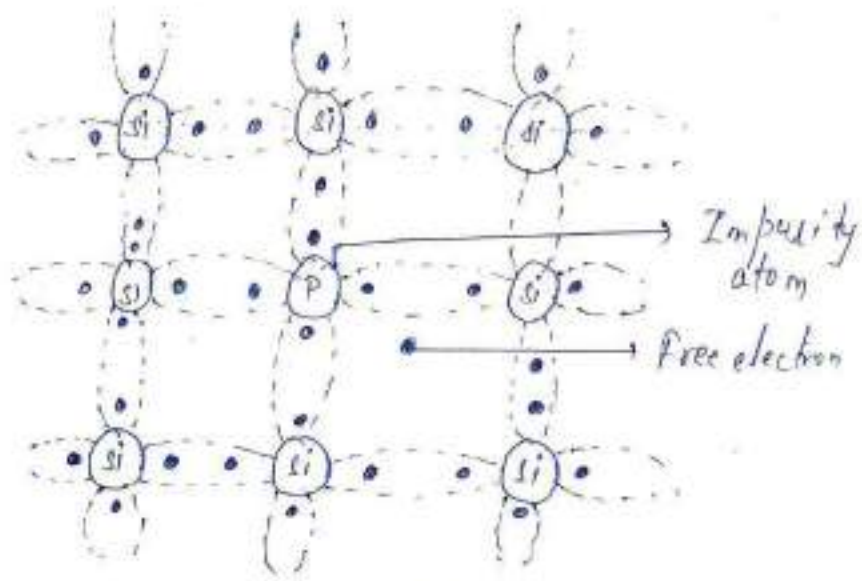


Fig. 8- A pentavalent impurity Atom (P) in a Si crystal.

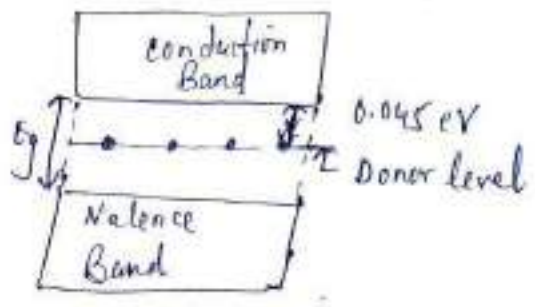


Fig. 9 Energy level diagram for N-Type Semiconductor

A small but definite amount of energy is required to detach this fifth electron from its nucleus and make it free to conduct. The energy required is however quite small as compared to the energy required for breaking a covalent bond and can be easily provided by thermal agitation inside the crystal.

The energy level corresponding to the fifth valence e^- lies in the band gap just below the conduction band edge as shown in fig (2). This energy level is called as donor energy level. The depth of this energy level is 0.045 eV for Si and 0.01 eV for Ge.

Each pentavalent impurity donates one free electron to the semiconductor therefore called as n-type or donor impurities and semiconductor containing such impurities are called as n-type semiconductor.

Acceptor or P-type Semiconductor \Rightarrow When a

trivalent impurity is added to a semiconductor, the resulting semiconductor is called as a p-type semiconductor. Let us consider that impurity of boron is added to Si. The three of the valence electrons of boron atom form covalent bonds with the three neighbouring silicon atom while the fourth bond is not completed due to deficiency of one electron. This deficiency is called as hole. Thus trivalent impurity atom has

a tendency to accept one electron from neighbouring Si atom to complete the fourth bond. This process requires a small amount of energy which is easily provided by the thermal agitation in the crystal. The transferred electron leaves behind a hole at its previous position on the Si-atom which acts as a current carrier.

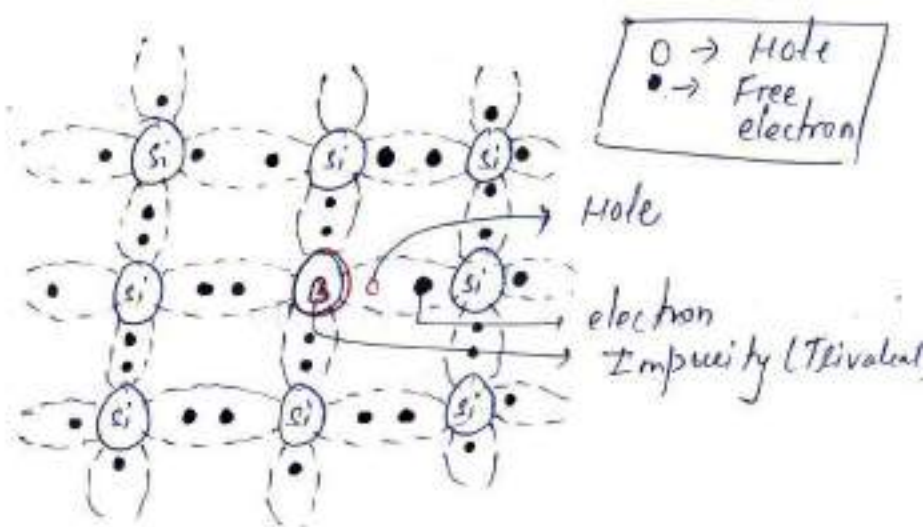


Fig:3 A trivalent impurity atom (Boron) in Si crystal

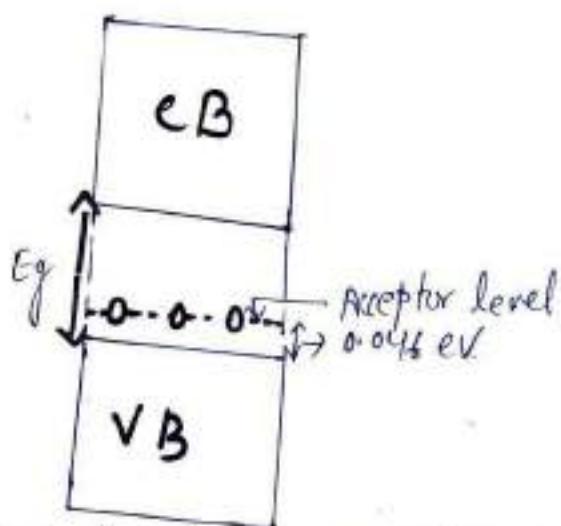


Fig:4 Energy level diagram of p-type semiconductor.

Each trivalent impurity atom can accept an electron from a neighbouring Silicon atom to produce a hole in the semiconductor. Such impurities are therefore known as acceptor or p-type impurities and semiconductor containing such impurities atoms is called as p-type semiconductor.

* In n-type of semiconductors electrons are majority carriers and in p-type of semiconductors holes are majority carriers. ∴

Effect of temperature on the conductivity of n-type and p-type semiconductor: →

Conductivity of n- and p-type semiconductor is directly proportional to temperature.

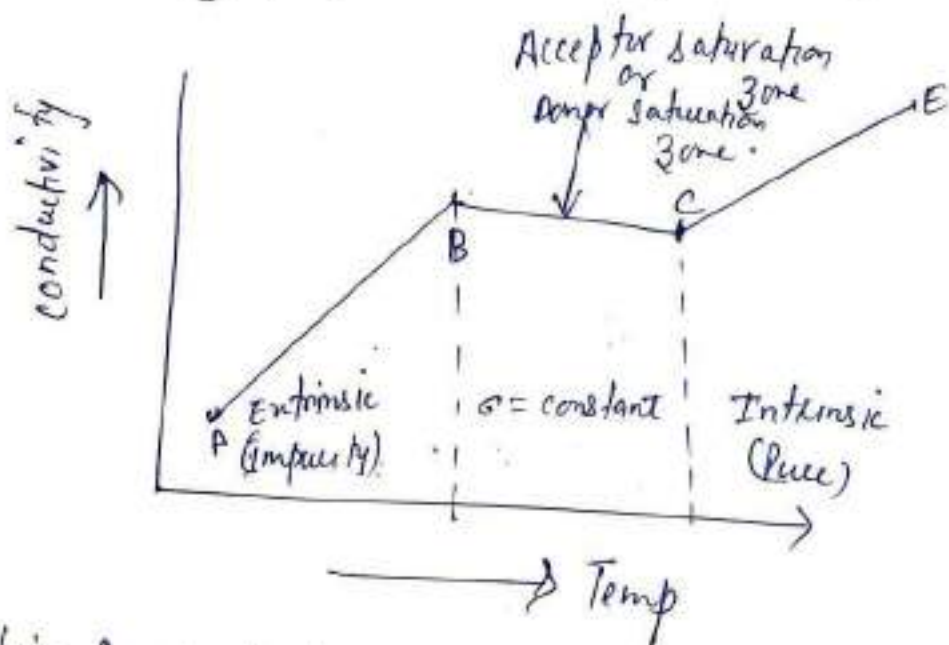


Fig. 5 Variation in conductivity of n-type and p-type semiconductor with rise in temp.

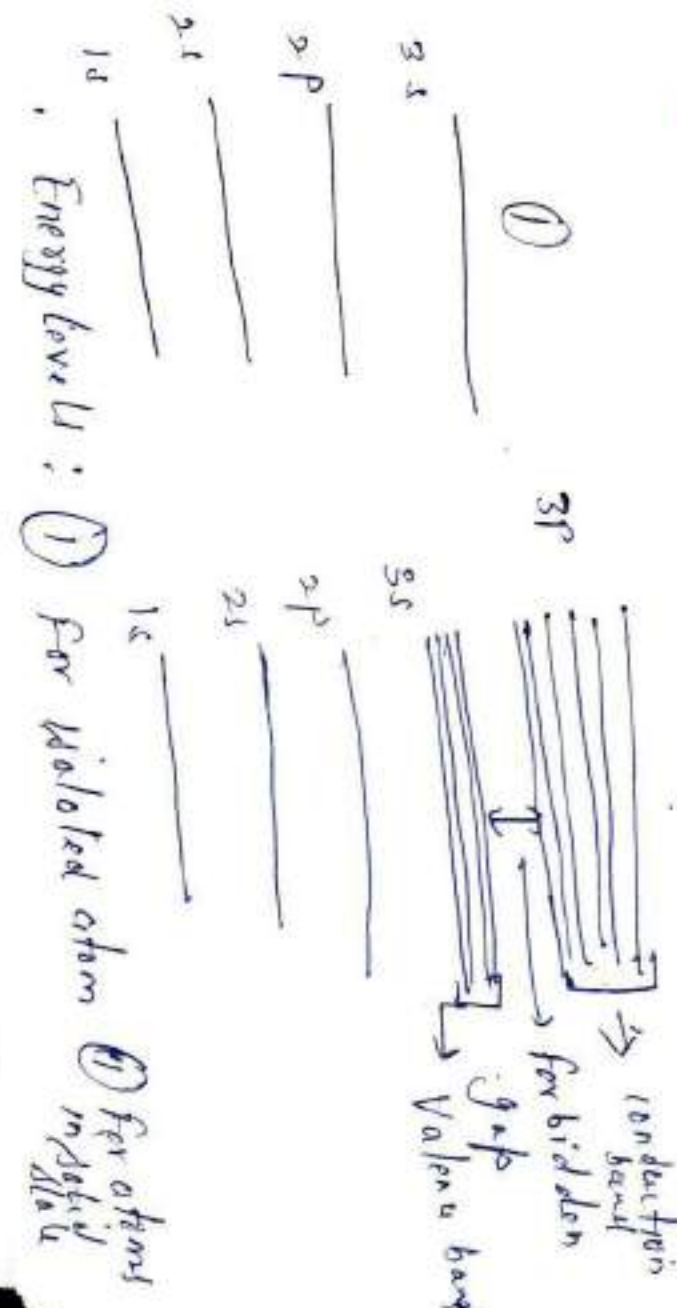
Band Structure of Solids & - Molecular Orbital

Theory extended to solids is known as **Band Theory of Solids**.

According to Band theory of solids because of very large number of atoms that interact in a solid material, the energy levels are so closely spaced that they form bands. The highest energy filled band, also known as **(HOMO)** is known as **valence band**.

The next higher band which is known as **(LUMO)** in a molecule (unoccupied molecular orbital) is known as **conduction band**.

The energy separation b/w conduction band and valence bands is known as **forbidden bands**.



METAL-LIGAND BONDING IN TRANSITION METALS COMPLEXES

The configuration (1) will be preferred when $\Delta_o > P$. These complexes are known as strong field complexes since Δ_o is large. The complex in this case has lesser number of unpaired electrons and is called **low spin** complex.

The configuration (2) is preferred if $\Delta_o < P$. These complexes are known as **weak field** complexes since Δ_o is not large. The complex in this case has maximum number of unpaired electrons and the complex is called **high spin** complex.

It may be concluded that if :

$$\Delta_o > P \text{ (strong field) : low spin complex}$$

$$\Delta_o < P \text{ (weak field) : high spin complex}$$









Therefore for low spin complex with t_{2g}^4 configuration CFSE = $4(-4Dq) = -16Dq$.

Taking into consideration the pairing energy, the net CFSE in this case = $-16Dq + P$. For a high spin complex with $t_{2g}^3 e_g^1$ configuration with $t_{2g}^3 e_g^1$ configuration

$$\text{CFSE} = 3(-4Dq) + 1(6Dq) = -6Dq$$









For d^4 , d^5 , d^6 and d^7 systems there can be two possibilities depending on the magnitude of crystal field splitting energy, Δ_o and pairing energy of the electrons P i.e. whether it is a case of strong field (low spin) or a weak field (high spin). In the table 1 given below are enlisted the configurations with their CFSE.

Table 1. CFSE of d^4 to d^7 configurations in octahedral field

Number of electrons	Weak field	CFSE	Strong field	CFSE
d^4	e_g 	$-6Dq$ Or $-0.6\Delta_o$	e_g 	$-16Dq + P$ Or $-1.6\Delta_o + P$
d^5	t_{2g} 	0	e_g 	$-20Dq + 2P$ $-2.0\Delta_o + 2P$
d^6	e_g 	$-4Dq$ Or $-0.4\Delta_o$	e_g 	$-24Dq + 2P$ Or $-2.4\Delta_o + 2P$
d^7	t_{2g} 	$-8Dq$ Or $-0.8\Delta_o$	e_g 	$-18Dq + P$ Or $-1.8\Delta_o + P$

For systems d^1 , d^2 , d^3 and d^8 , d^9 , d^{10} , the number of unpaired electrons is fixed. There is only one way of filling the d -orbitals to attain minimum energy irrespective of the field.

Table 2. CFSE of d^1 to d^3 and d^7 to d^8 configuration in octahedral field.

Number of electrons	Weak or Strong field	CFSE	Number of electrons	Weak or Strong field	CFSE
d^1		$-4Dq$ or $-0.4\Delta_o$	d^8		$-12Dq$
d^2		$-8Dq$	d^9		$-6Dq$
d^3		$-12Dq$	d^{10}		0
		$-12\Delta_o$			$-6.6\Delta_o$

It may be noted here that the difference between the CFSE values of strong field and the weak field shall determine whether the high spin or low spin will be preferred for d^4 to d^7 systems. There are $(-10Dq + P)$, $(-20Dq + 2P)$, $(-20Dq + 2P)$ and $(-10Dq + P)$ respectively for d^4 , d^5 , d^6 and d^7 system as shown below :

Table 3. Difference in CFSE between strong and weak field cases.

Number of electrons	CFSE weak field	CFSE strong field	Difference
d^4	$-6Dq$	$-16Dq + P$	$-10Dq + P$
d^5	0	$-20Dq + 2P$	$-20Dq + 2P$
d^6	$-4Dq$	$-24Dq + 2P$	$-20Dq + 2P$
d^7	$-8Dq$	$-18Dq + P$	$-10Dq + P$

The configurations d -orbitals in complexes may be noted in notations quite similar to one used for the electronic configuration of atoms and ions. The occupied orbital is denoted by symbol t_{2g} or e_g with the right superscript to indicate the number of electrons occupying that orbitals. For example d^5 high spin complex is given the electronic configuration $t_{2g}^3 e_g^2$ and the low spin complex is given the electronic configuration t_{2g}^5 .

★ 4. Crystal Field Splitting in Tetrahedral Complexes

Let us now consider the crystal field splitting of d -orbitals in a tetrahedral complex. Since the tetrahedron has quite a different symmetry from the octahedron we need a new diagram to show the relationship between the positions of the ligands and the direction of the d -orbitals. To obtain this, we may visualise the tetrahedral arrangement as being made by joining two pairs of opposite corners of opposite faces of the cube to the centre where the metal atoms sits through which the x , y and z axes pass so that they are perpendicular to the cube faces as shown in fig. 6.

None of the d -orbitals now points exactly at the ligands and hence the approach of the ligands as shown in fig. 6 does not coincide with either set of orbitals. The angle between e_g set of orbitals of the