Q.1. What is Crystal Field Theory? How it different from Valence Bond Theory?

Ans:-

Crystal Field Theory ↓	Valence Bond Theory ↓
CFT is a model that is designed to explain the breaking of degeneracies of electron orbitals due to static electric field produced by a surrounding anion or anions (or legands).	VBT is a theory that explains the formation of a covalent bond via hybridization of atomic orbitals.
CFT explains the splitting of orbitals.	VBT explains the mixing of orbitals.

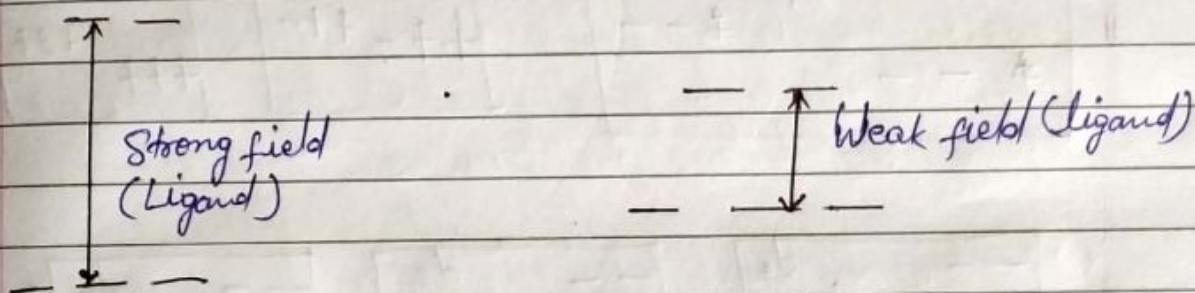**Q.2.** Explain crystal field splitting of d-orbitals in octahedral complexes.

Ans→
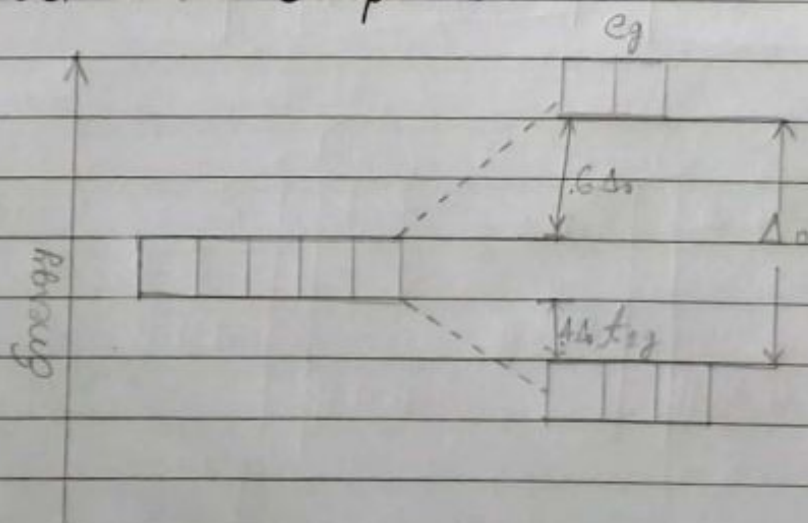
e_g = The higher energy set of orbitals (d_{z^2} and $d_{x^2-y^2}$)

t_{2g} = The lower energy set of orbitals (d_{xy}, d_{yz} & d_{xz})

Δ_0 or $10\,Dq$ = The energy separation between the two levels

The e_g orbitals are repelled by an amount of $0.6\,\Delta_0$
The t_{2g} orbitals to be stabilized to the extent of $0.4\,\Delta_0$

Strong field
(Ligand)

Weak field (Ligand)

Here Δ_0 for strong ligand is greater than weak field (ligand).
∴ e^- can't easily jump to e_g from t_{2g} in strong field while it can jump easily in weak field (ligand).

As Δ_0 decreases, the stability of e^- increases in d-orbitals in octahedral complexes.

⇒ ~~Δ_0 (CFSE) for d-orbitals~~

CFSE = ~~for high-spin, $(3 \times 0.4) - ($~~

(no: of e^- in ~~t_{2g}~~ low energy level) × ($-4\,Dq$)
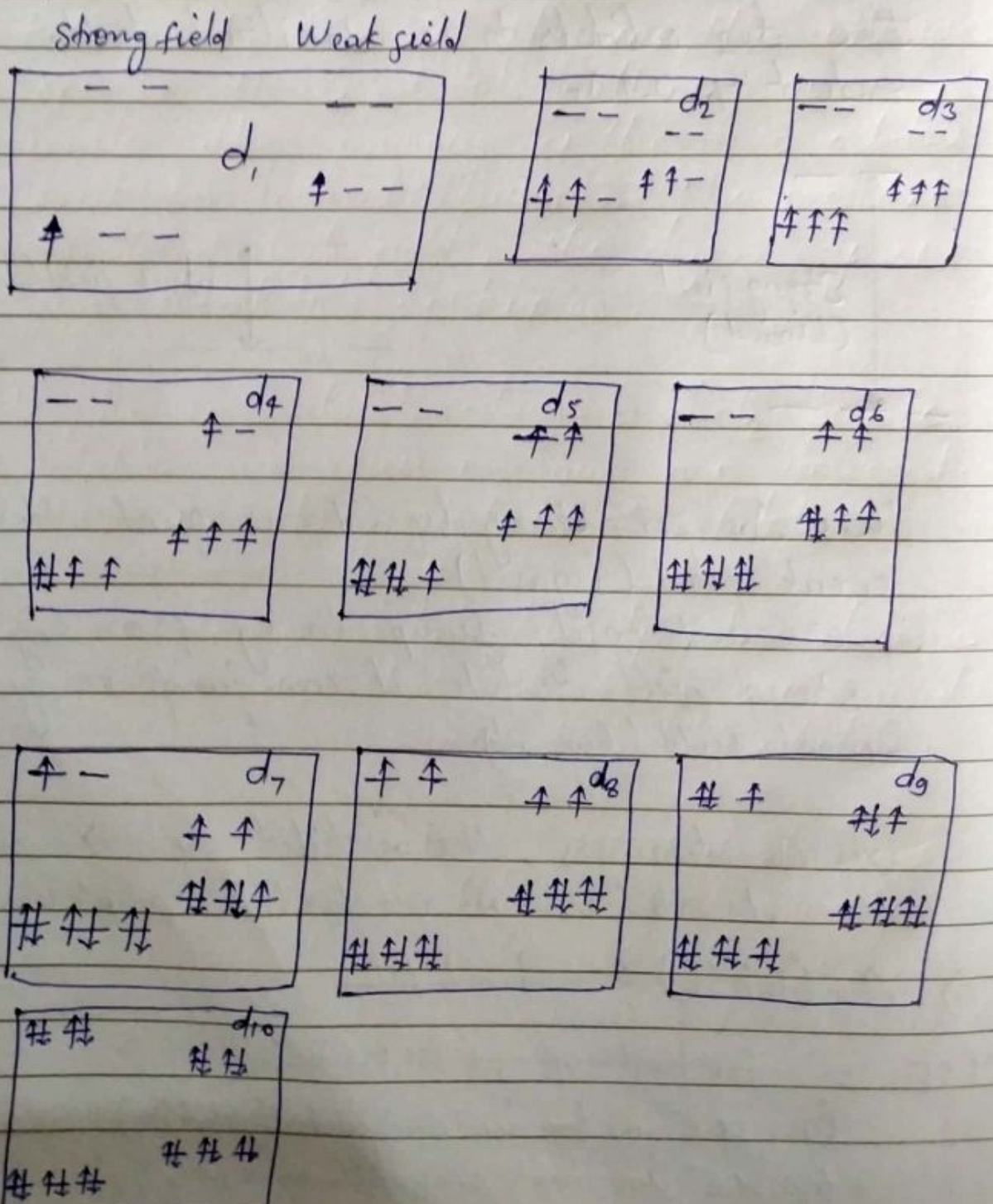+ (no. of e^- in high energy level) × ($+6\,Dq$)

$$CFSE(\Delta_0) = \text{no. of } e^- \text{ in } t_{2g} \times (.4\Delta_0)$$
$$- \text{no. of } e^- \text{ in } e_g \times (.6\Delta_0)$$

$$\Delta_{0x} < \Delta_{0y}$$
$$\text{Stability}_x > \text{Stability}_y$$

Some Examples :-

Strong field   Weak field

Q.3. Why do transition elements form coloured compounds? Explain.

Ans) The transition elements have the property to absorb certain radiations from the visible region of the spectrum and as a result, the transmitted or reflected light is coloured.

In the case of transition metals complexes, the energy difference between t_{2g} and e_g sets of d-orbitals is very small. When visible light falls on them, the electron gets raised from lower set of orbitals to higher set of orbitals (for example in case of octahedral complexes, the e^- goes to e_g from t_{2g}). As a result of absorption of some selected wavelength of visible light corresponding to energy difference between t_{2g} to e_g energy levels, the transmitted light gives colour to complexes.

Q.4. Discuss the crystal field splitting of d-orbitals in tetrahedral complexes.

Ans)
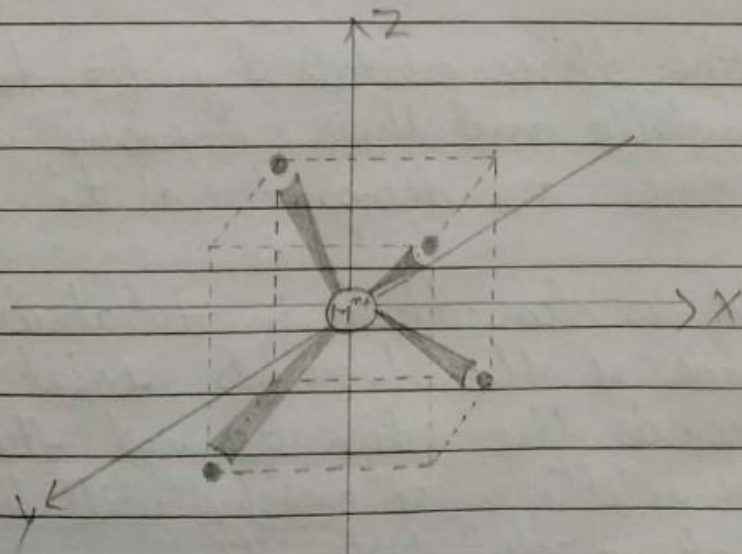
It is clear that the orbitals d_{xy}, d_{yz} and d_{zx} points between X, Y and Z-axis (i.e. towards the centre of of the edges of the cube) whereas the orbitals $d_{x^2-y^2}$ and d_{z^2} point along x, y and z axis (i.e. to the centres of the faces of the cube). The three d-orbitals d_{xy}, d_{yz} and d_{zx} are pointing close to the direction in which the ligands are approaching while the two orbitals $d_{x^2-y^2}$ and d_{z^2} are lying in between the ligands. Therefore, the energies of the three orbitals will be raised while the energies of the two orbitals will be lowered. Thus, in the presence of tetrahedral field, the degeneracy of five d-orbitals split-up as:-
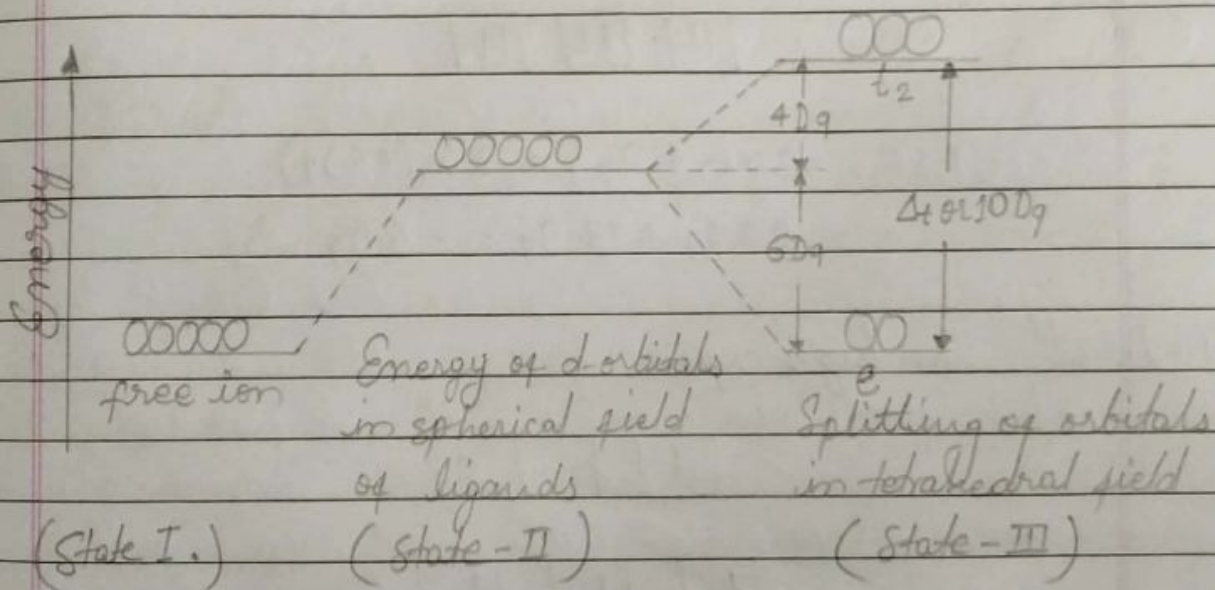
(i) The two orbitals, $d_{x^2-y^2}$ and d_{z^2} become stable and their energies are lowered. These are designated as 'e' orbitals.

(ii) The three orbitals d_{xy}, d_{yz}, d_{zx} become unstable and their energies are raised. These are designated as 't_2' orbitals.

Note:- 1. It is clear that in tetrahedral field, none of the d-orbitals point exactly towards the ligands and therefore, the splitting of energy will be less than that in octahedral field.

Note 2. It may be noted that for the splitting of d orbitals in tetrahedral field, the subscript 'g' is not used. For example, the orbitals $d_{x^2-y^2}$ and d_{z^2} are designated as 'e' orbitals whereas the other three orbitals d_{xy}, d_{yz} and d_{zx} are designated as t_2. This is because a tetrahedral geometry has no centre of symmetry. The symbols 'g' and 'u' have meaning only for fields which have centre of symmetry.

free ion	Energy of d orbitals in spherical field of ligands	Splitting of orbitals in tetrahedral field
(State I.)	(State - II)	(State - III)

Crystal field splitting in a tetrahedral field.

Q.5. Calculate CFSE for following :-
(i) d^5 strong field octahedral
(ii) d^3 weak field octahedral
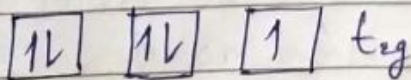(iii) d^4 high spin & low spin (octahedral)

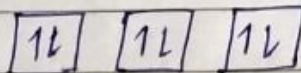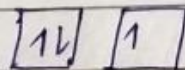(iv) d^5 tetrahedral
(v) d^6 tetrahedral

Soln: (i):- d^5 ☐ ☐ e_g

strong field
octahedral $\boxed{1\downarrow}$ $\boxed{1\downarrow}$ $\boxed{1}$ t_{2g}

∴ CFSE = $5 \times (-4Dq) + 0 \times (+6Dq)$

= $-20\,Dq$ Ans

(ii) d^9 $\boxed{1\downarrow}$ $\boxed{1}$

$\boxed{1\downarrow}$ $\boxed{1\downarrow}$ $\boxed{1\downarrow}$

CFSE = $6 \times (-4\,Dq) + 3 \times (+6Dq)$

= $-24\,Dq + 18\,Dq = -6\,Dq$ Ans

(iii) d^4 in high spin

$\boxed{1}$ ☐ e_g

$\boxed{1}$ $\boxed{1}$ $\boxed{1}$ t_{2g}
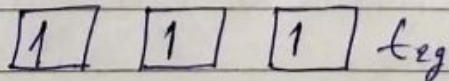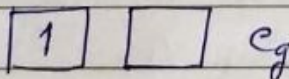
CFSE = $3 \times (-4Dq) + 1 \times (+6\,Dq)$

= $-12\,Dq + 6\,Dq = -6\,Dq$ Ans.

d^4 in low spin: ☐ ☐ e_g

$\boxed{1\downarrow}$ $\boxed{1}$ $\boxed{1}$ t_{2g}
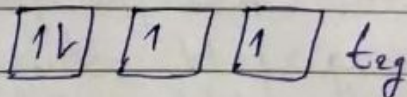
CFSE = $4 \times (-4\,Dq) + 0 \times (6\,Dq) = -16\,Dq$ Ans

(iv) d^5 tetrahedral :- | 1 | 1 | 1 | t_2

| 1 | | 1 | e
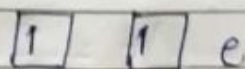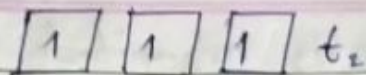
$$CFSE = 2 \times (-6) + 3 \times (+4) = (-12 + 12) \, Dq$$
$$= 0 \, Dq \quad \underline{Ans.}$$

(v) d^6 tetrahedral :- | 1 | 1 | 1 | t_2

| 1↿ | | 1 | e
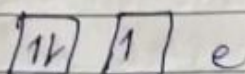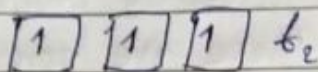
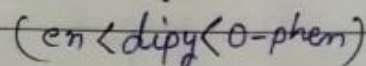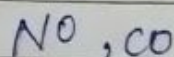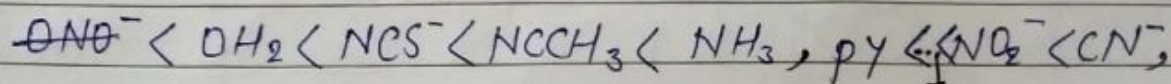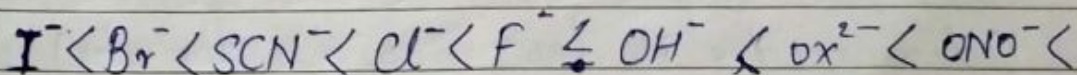$$CFSE = 3 \times (-6 Dq) + 3 \times (+4 Dq) = -18 Dq + 12 Dq$$
$$= -6 Dq \quad Ans.$$

Q.6. What is spectrochemical series?

Ans: Spectrochemical series gives the arrangement of ligands in the increasing order of crystal field splitting.

Weak field ligands cause less crystal field splitting. They form high spin complexes. Examples include chloride ions, fluoride ions etc. Strong field ligands cause greater crystal field splitting. They form low spin complexes. Examples includes cyanide ion and CO.

$$I^- < Br^- < SCN^- < Cl^- < F^- \lessapprox OH^- < ox^{2-} < ONO^- <$$

$$\cancel{ONO^-} < OH_2 < NCS^- < NCCH_3 < NH_3, \, py \lessapprox NO_2^- < CN^-,$$

$$(en < dipy < o\text{-phen})$$

$$NO, \, CO$$

(weak) Increasing ligand field strength (strong)

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Q.7. Why is magnitude of Δ_t less than Δ_o?

Ans→

$$\Delta t = \frac{4}{9} \Delta_o$$

There are two main reasons for $\Delta_t < \Delta_o$:-

(i) In tetrahedral complexes, there are four ligands while there are six ligands in octahedral complexes. Therefore, lesser ligands produce less crystal field splitting. The crystal field splitting in tetrahedral field is about 2/3 of the octahedral field.

(ii) In tetrahedral field, none of the orbitals is pointing directly towards the ligands and therefore splitting is less.

Q.8. Why $[CoF_6]^{3-}$ is paramagnetic but $[Co(NH_3)_6]^{3+}$ is diamagnetic though both are octahedral?

Ans(i) If $P > \Delta_o$, the electron will not pair up and the complex will be high spin complex as well as the complexes with weak ligand field (paramagnetic).

(ii) If $\Delta_o > P$, the electrons will prefer to pair up and the complex will be low spin complex (diamagnetic or low magnetic character) with strong ligand field.

$[CoF_6]^{3-}$

Δ_0 (small value)

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

Δ_0 (Large Value)

High spin complex
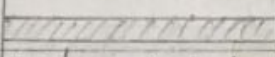(Paramagnetic)

low spin complex
(Diamagnetic)
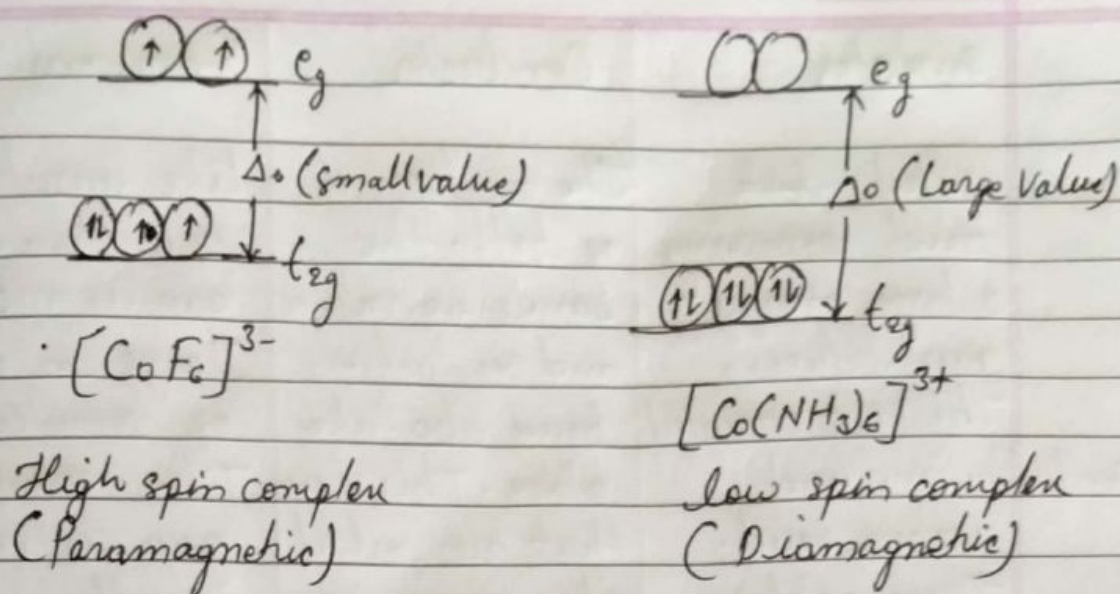
Cobalt in $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$ is in +3 oxidation state and it has six d electrons.
It has been observed that F^- ion is a weak field ligand and $\therefore \Delta_0$ is smaller than P.
On other hand, NH_3 is a strong field ligand and so, Δ_0 is greater than P.
Therefore $[CoF_6]^{3-}$ complex is paramagnetic due to presence of 4 unpaired e^- because of $\Delta_0 < P$, and $[Co(NH_3)_6]^{3+}$ complex is diamagnetic due to presence of electron pair because of $\Delta_0 > P$.

Q.9. On the basis of band theory, differentiate between insulator, conductor and semiconductor.

Ans)

Insulator	Conductor	Semiconductor
A solid having each occupied band completely	Electrons fill the conduction band partially.	The conduction band is empty and the valence band is fully filled with e.

Insulator	Conductor	Semiconductor
filled but and possessing a large energy gap between highest occupied Conduction band and valence band. There exist a large forbidden zone.	The overlapping of both the bands i.e. valence and conduction band also take place. This shows that no forbidden energy gap is present.	Like insulators, forbidden energy gap is not so large in case of semi-conductor. The energy gap is very small.
Conduction Band		Conduction Band
	Conduction Band	
	Valence Band	Valence Band
Valence Band		

Q.10. Differentiate between n-type semiconductor and p-type semiconductor.

(Ans)

n-type semiconductor	p-type semiconductor
It is type of extrinsic semiconductor	It is also type of extrinsic semiconductor.
In n-type semiconductor, electrons are majority carriers and holes are minority carriers.	In p-type semiconductor, holes are majority carriers and electrons are minority carriers.

n-type semiconductor	p-type semiconductor
It has larger e⁻ concentration and less hole concentration	It has larger hole concentration and less e⁻ concentration.
Pentavalent impurities are added.	Trivalent impurities are added.
It has donor energy levels very close to conduction band.	It has acceptor energy level very close to valance band.