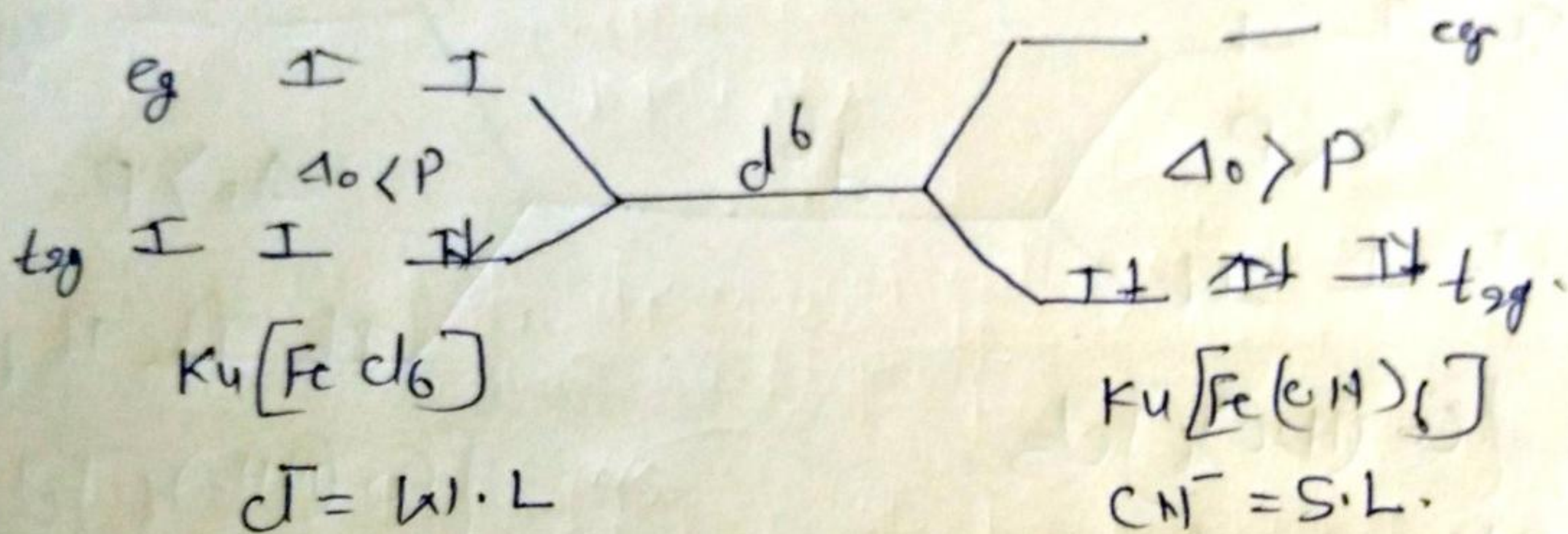


Q  $K_4[FeCl_6]$  is Paramagnetic but  $K_4[Fe(CN)_6]$  is diamagnetic. Why?

→  $K_4[FeCl_6] = Fe(II)$   
 $K_4[Fe(CN)_6] = Fe(II)$  }  $d^6$  system.



$\bar{Cl}$  is a weak ligand so it causes small splitting in the O.C and so  $\Delta_0 < P$ , but  $CN^-$  is a strong ligand so it causes large extent of splitting and hence  $\Delta_0 > P$

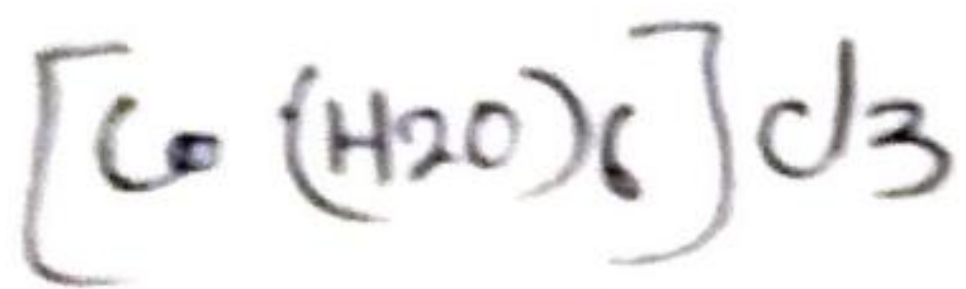
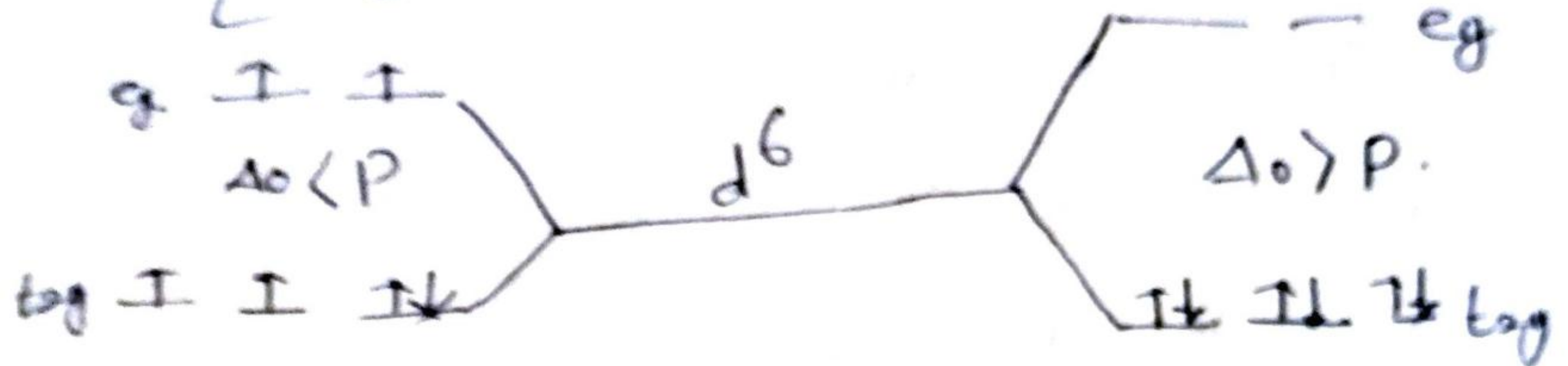
$K_4[FeCl_6]$   
 $n = 4$   
 Paramagnetic  
 $\mu_s = \sqrt{4(4+2)} \text{ BM}$   
 $= 2\sqrt{6} \text{ BM}$

$K_4[Fe(CN)_6]$   
 $n = 0$   
 Diamagnetic  
 $\mu_s = 0$

$NH_3$  behaves as a strong ligand in case of  $d^6$  systems so  $\Delta_0 > P$  favouring the formation of spin paired Oh complexes. Thus there is no unpaired electrons, it is diamagnetic. But in case of  $d^5$ ,  $d^7$  and  $d^8$   $NH_3$  can not pair electrons

Q.  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  is diamagnetic but  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$  is paramagnetic. Explain.

→  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 = \text{Co(III)}$   
 $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3 = \text{Co(II)}$  }  $d^6$  system.



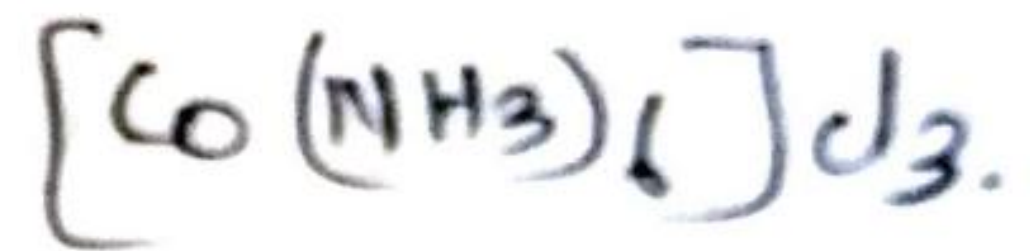
Spin free/High spin

$n = 4$

Paramagnetic

$\mu_s = \sqrt{4(4+2)} \text{ BM}$

$= 2\sqrt{6} \text{ BM}$



Spin paired/Low spin.

$n = 0$

Diamagnetic

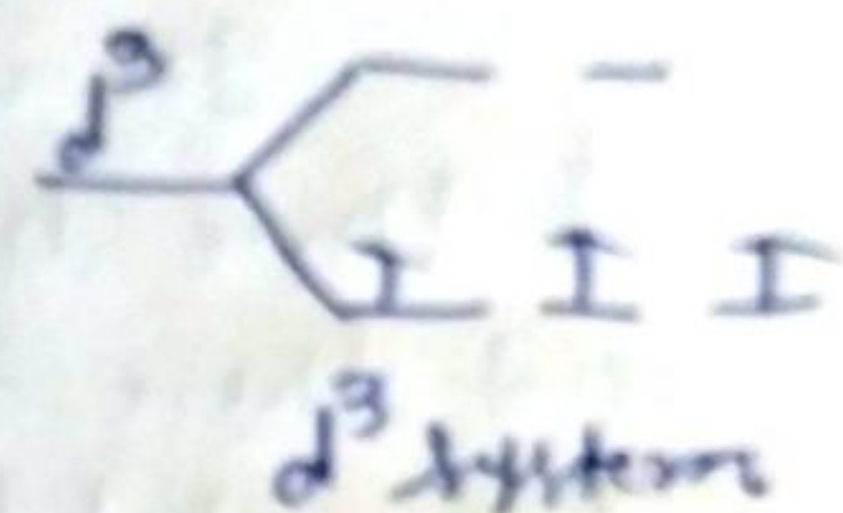
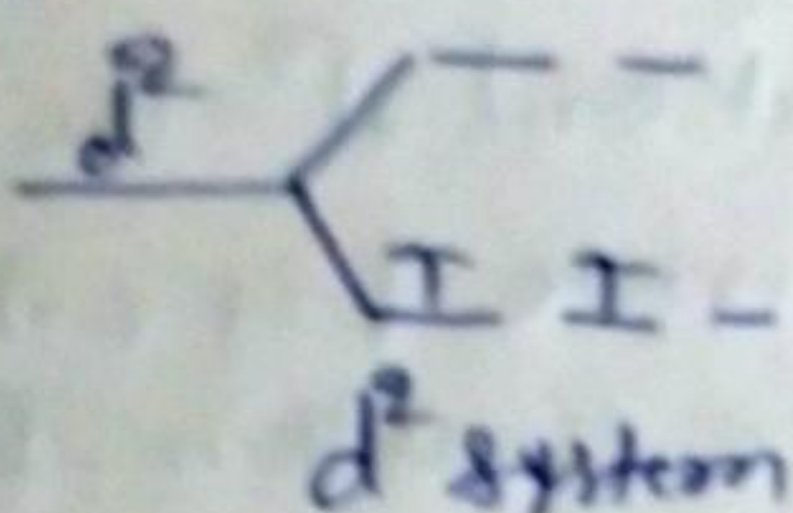
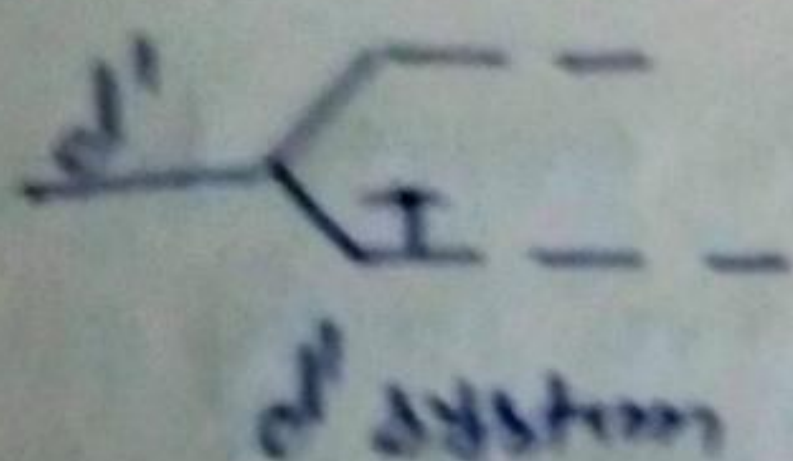
$\mu_s = 0$

$\text{NH}_3$  is a strong ligand it causes large extent of ~~orbital~~ splitting in the d-orbitals and hence  $\Delta_0 > P$ . That's why electrons are forced to pair up and is called spin paired or low spin oh. complex.

Whereas  $\text{H}_2\text{O}$  is a very weak ligand causes small splitting hence  $\Delta_0 < P$ . That's why electrons are unpaired and this is referred to as spin free or high spin oh. complex.

Q.  $d^1, d^2$  and  $d^3$  systems form only spin free octahedral complexes (O.C) while  $d^4, d^5, d^6$  and  $d^7$  systems form both spin free and spin paired octahedral complexes.  
Explain.

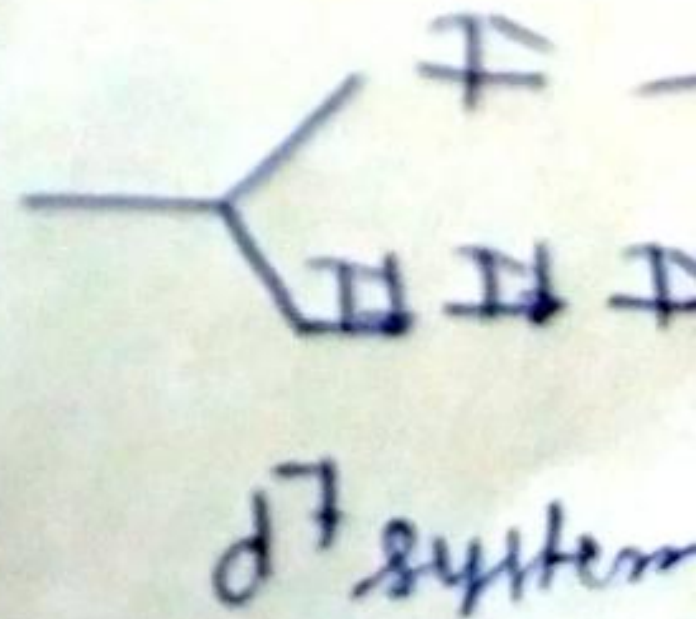
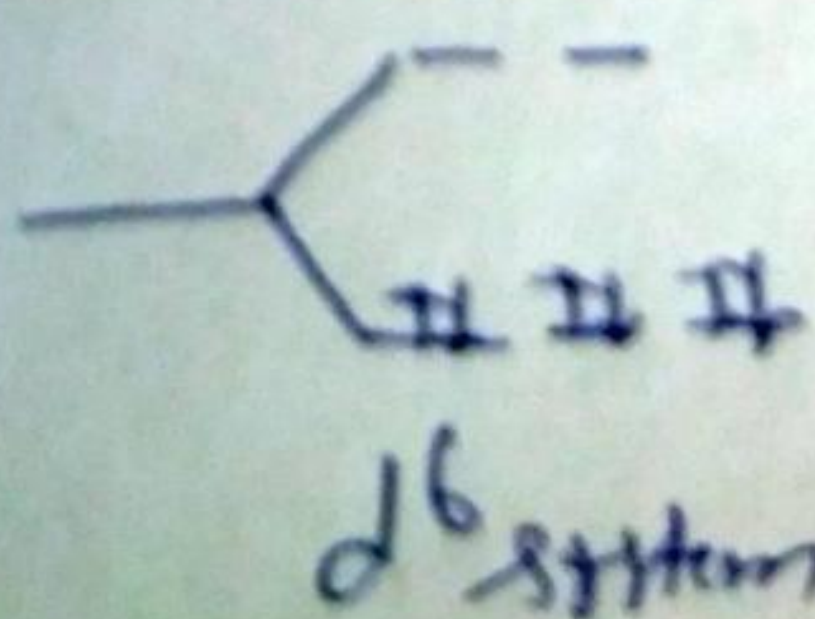
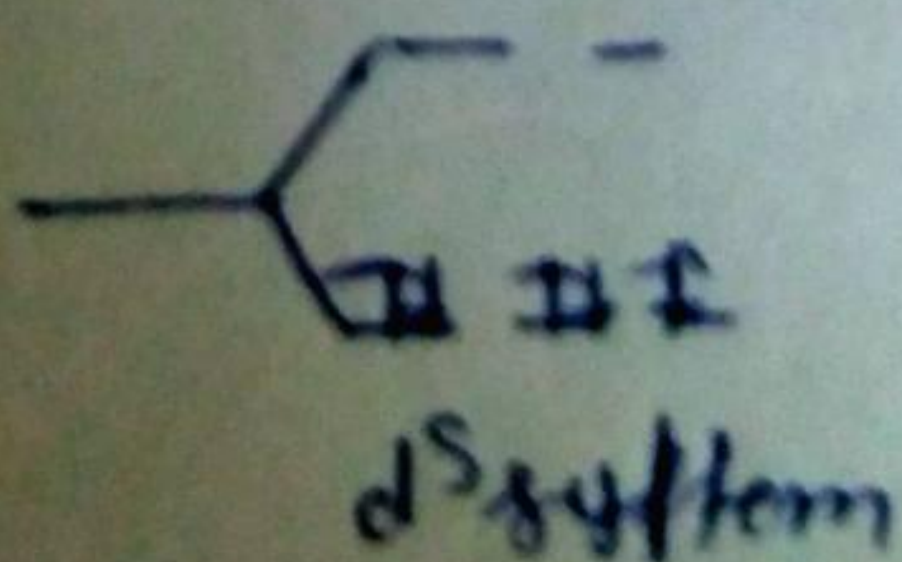
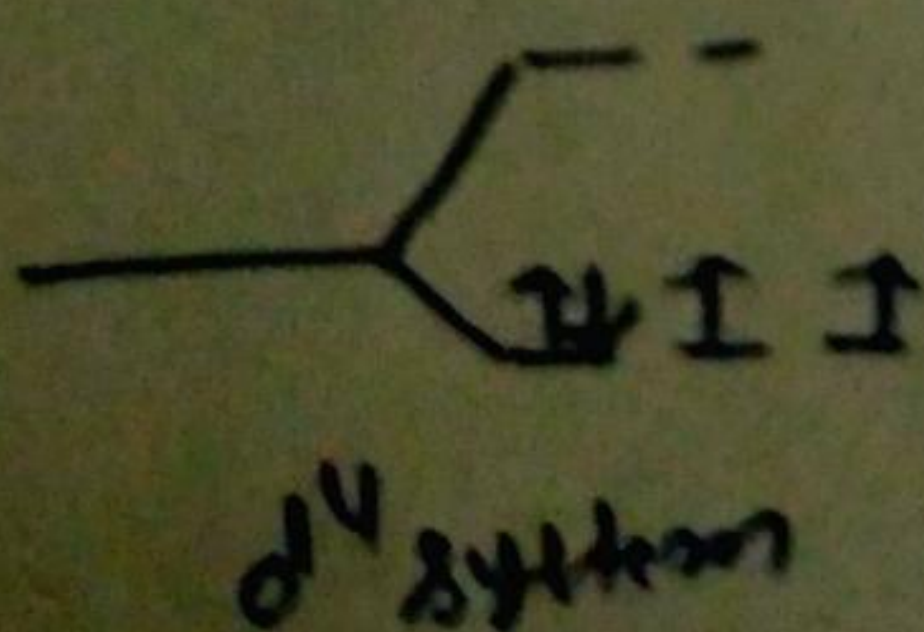
→ In splitting of octahedral complex ~~there~~ three d-orbitals i.e.  $d_{xy}, d_{xz}$  and  $d_{yz}$  have lower energy than other two d-orbitals i.e.,  $d_{x^2-y^2}$  and  $d_{z^2}$ . So, d-electrons will first prefer to fill up the lower 3d-orbitals according to Hund's rule.



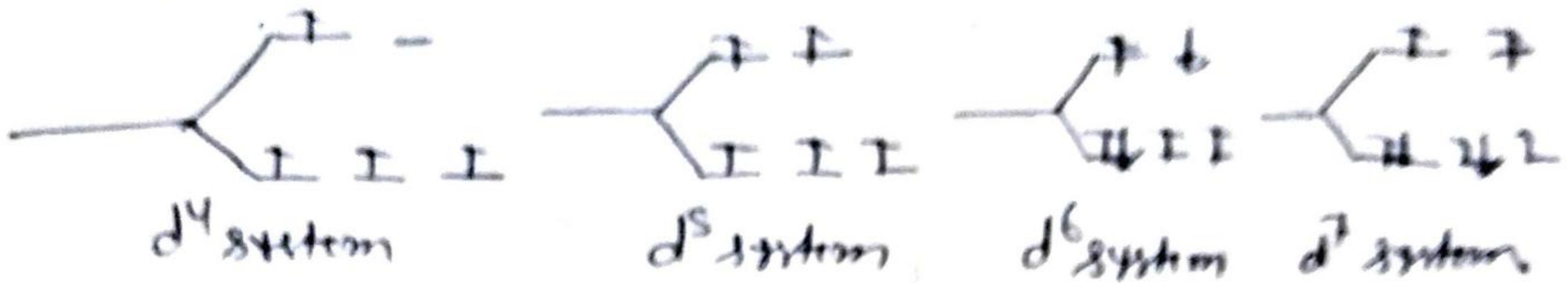
So,  $d^1, d^2$  and  $d^3$  systems are spin free or high spin octahedral complexes.

But in case of  $d^4, d^5, d^6$  and  $d^7$ , two cases arise i.e., either the electrons prefer to pair up or will go to orbitals with high energy. Now this case depends upon two factors they  $\Delta_0$  (crystal field splitting energy) and  $P$  (pairing energy).

If  $\Delta_0 > P$ , then electrons prefer to pair up and thus forming spin paired or low spin octahedral complexes.



Similarly if  $\Delta_0 < P$ , then electron prefers to go to orbitals of higher energy rather pairing up. And so electrons are filled in all the five d orbitals by Hund's rule. So they are called spin free or high spin octahedral complex.



In  $d^1$ ,  $d^2$  and  $d^3$  the lower energy level consisting of three degenerate  $t_{2g}$  orbitals are singly occupied and there is no question of pairing of electron in  $t_{2g}$  orbitals so they form only spin free complexes. But in  $d^4$ ,  $d^5$ ,  $d^6$  and  $d^7$  system after the single occupation of  $t_{2g}$  electron the next electron may pair up in  $t_{2g}$  or go to  $e_g$  depending on relative values of  $\Delta_0$  and  $P$ , the fourth electron prefers to go to  $e_g$  and remain unpaired thus they are capable of forming both spin free and spin paired Oh. complexes.