

## CRYSTAL FIELD THEORY (CFT)

There are mainly three theories which are used to describe the nature the nature of metal-ligand bonding in coordination compounds.

1. **Valence Bond Theory (VBT):** VBT was developed by **Linus Pauling** and Others in 1930.
2. **Crystal Field Theory (CFT):** CFT was proposed by **Hans Bethe** in 1929.
3. **Ligand Field Theory (LFT) or Molecular Orbital Theory (MOT):** Developed by **J.H.Van Vleck** in 1935.

**Valence Bond Theory** was the first theory used to explain the geometry and magnetic property of many to coordination compounds. The basic idea of the theory is that the formation of a complex is a reaction between a **Lewis** base (ligand; electron donor) and a **Lewis** acid (metal or metal ion; electron acceptor) with the formation of a coordinate-covalent bond (dative bond) between the ligand and the metal. This is based on following assumptions:

1. The central **metal atom or ion** provides number of **vacant s, p & d orbitals equal to its coordination number** to form coordinate bond with the ligand orbitals.
2. Each ligands has at least one  $\sigma$ -orbital containing a lone pair of electrons
3. The empty orbitals of the **metal atom or ion** undergo **hybridisation** to form same number of hybrid orbitals. These hybrid orbitals overlap with the filled  $\sigma$ -orbitals of the ligands to form ligand to metal coordinate  $\sigma$ -bond.
4. The **geometry** of complex ion depends on **hybridisation** of metal orbitals.

Types of hybridization	Geometry
$sp$ hybridisation	Linear
$sp^2$ hybridisation	Triangular planar
$sp^3$ hybridisation	Tetrahedral
$dsp^2$ hybridisation	Square planar
$dsp^3$ hybridisation	Trigonal bipyramidal
$d^2sp^3$ hybridisation	Octahedral
$d^3sp^3$ hybridisation	Pentagonal bipyramidal

- 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.

**Limitations of VBT :** The VBT reigned for a period of two decades in the realm of coordination chemistry because of its simplicity and ease in explaining structural and magnetic properties. It could adequately explain low-spin square-planar, high-spin tetrahedral and both low- and high-spin octahedral complexes. But with the progress of time following shortcomings were noticed with the VBT and it is now largely abandoned.

**Disadvantages:**

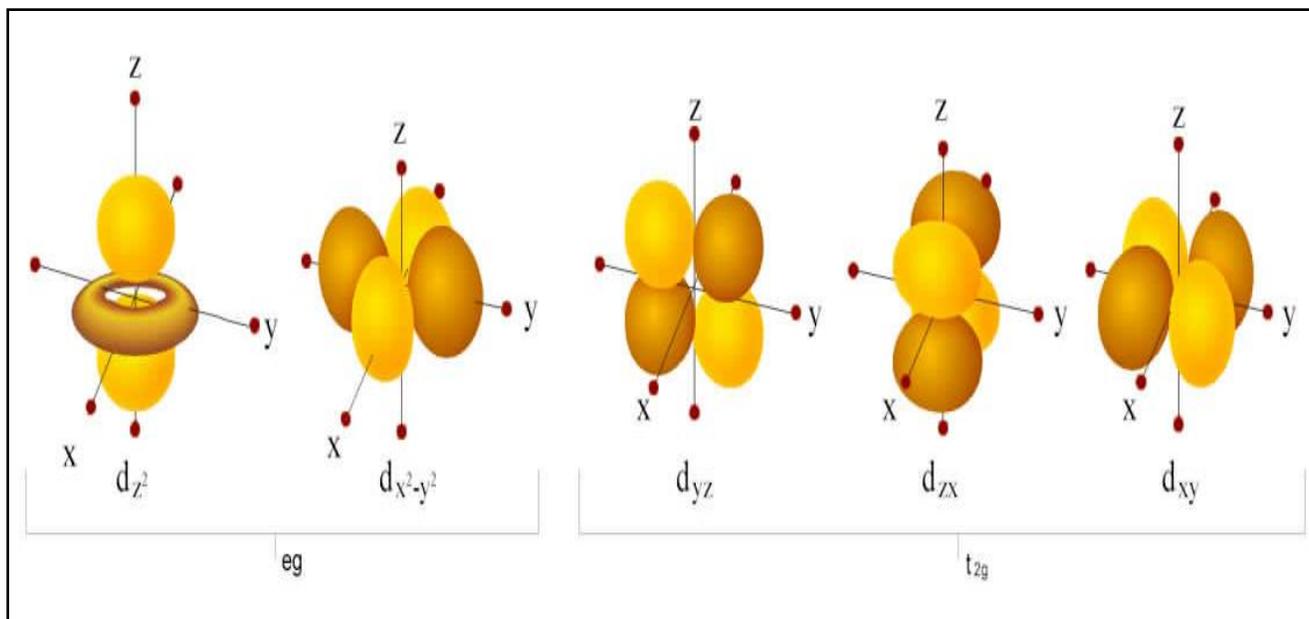
1. It fails to predict whether a 4-coordinate complex will be tetrahedral or square-planar and whether an octahedral complex will be low-spin or high-spin.
2. It fails to distinguish certain geometries like tetragonal or distorted octahedral.
3. It completely neglects excited states in a complex and can not explain absorption spectrum.
4. It doesn't have scope for quantitative calculation of bond energy and stability of complexes.
5. It does not adequately explain the magnetic data beyond specifying the number of unpaired electrons .
6. Too much stress has been given on metal ion while the importance of ligands is not properly addressed.

**Crystal Field Theory** was proposed by the physicist Hans Bethe in 1929 to describe the bonding in coordination complexes and to rationalize and predict some important properties of coordination complexes (colours, magnetism etc.). This model was based on a purely interaction between the ligands and the metal ion in the complexes with various geometries like octahedral, tetrahedral, square planar etc. Subsequent modifications were proposed by J. H. Van Vleck in 1935 to allow for some covalency in the interactions.

This theory is based on the concept that when the negative charges of the incoming ligands (or the negative ends of dipolar molecules like  $\text{NH}_3$  and  $\text{H}_2\text{O}$ ) attract the positively charged metal ion, there is also repulsive interaction between d electrons present on the metal ion and the ligands. Certain assumptions are taken while dealing with CFT-

1. The ligands are treated as point charges. In fact, this is not practically true since sometimes the size of ligand particularly when it is sulfur or phosphorus donating ligands, is approximately similar to the size of metal ion.
2. The interactions between metal ion and ligand are treated as purely electrostatic, no covalent interactions are considered. This again is not true, some of the observations cannot be explained without invoking covalent interactions. In isolated gaseous metal ion, all of the five d-orbitals are degenerate.
3. When a hypothetical spherical field of ligand approaches the metal ion, d-orbitals still remain degenerate, but their energy level is raised a bit due to repulsion between the orbitals of metal & ligand. This energy level is called Barycenter. But in the transition metal complexes, the geometry about the metal ions are octahedral, tetrahedral or square planar etc., the field provided by the ligands is not at all spherically symmetrical therefore d-orbitals are unequally affected by the ligands and degeneracy of d-orbitals in metal removed and split into different energy levels ( e.g.  $t_{2g}$  or  $e_g$ ).

To understand CFT, it is essential to understand the description of the lobes of d-orbitals (given in the **Figure1**):

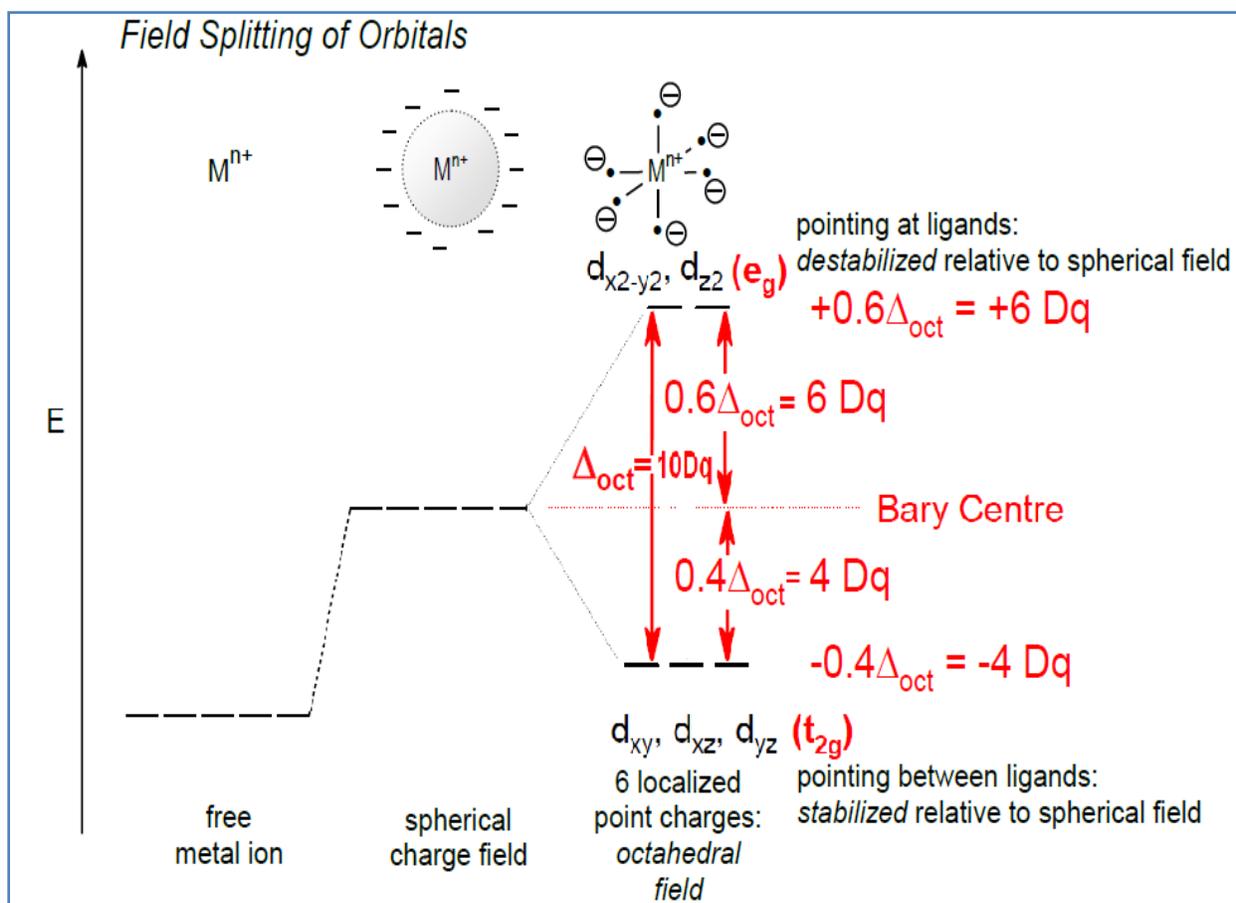


- $d_{xy}$ : lobes lie in-between the x and the y axes.
- $d_{xz}$ : lobes lie in-between the x and the z axes.
- $d_{yz}$ : lobes lie in-between the y and the z axes.
- $d_{x^2-y^2}$ : lobes lie on the x and y axes.
- $d_{z^2}$ : there are two lobes on the z axes and there is a donut shape ring that lies on the xy plane around the other two lobes.

*Figure 1: Shapes of d-orbitals*

## CRYSTAL FIELD EFFECTS ON OCTAHEDRAL COMPLEXES

- In octahedral complexes, the ligands approach along the axes.
- The d-orbitals where electron density is oriented along the axes,  $d_{x^2-y^2}$  and  $d_{z^2}$  are repelled much more by the ligands while the orbitals  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$  having electron density oriented in between the axes are repelled lesser by the ligands.
- Two sets of orbitals eg (doubly degenerate set) and  $t_{2g}$  (doubly and triply degenerate) are formed due the repulsion between metals and ligands orbitals.



a, b = singly degenerate labels  
 e = doubly degenerate  
 t = triply degenerate

g = gerade (symmetrical about origin)  
 u = ungerade (unsymmetrical about origin)

**Figure2: Splitting of d-orbitals in Octahedral Field**

- The energy gap between  $e_g$  and  $t_{2g}$  is called **crystal field splitting energy** and it is denoted by  $\Delta_o$  or  $\Delta_{oct}$  or  $10Dq$ , where  $\Delta$  represent **Crystal field splitting energy**, "o" in  $\Delta_o$  is for octahedral.
- Because the overall energy is maintained, the energy of the three  $t_{2g}$  orbitals are lowered or stabilised by  $0.4 \Delta_o$  and the energy of the two  $e_g$  orbitals are raised or repelled by  $0.6\Delta_o$  with respect to hypothetical the spherical crystal field or Bary Centre.

The  $Dq$  notation has mathematical origins in CFT but  $\Delta_o$  is preferred because of its experimentally determined origin.

The size of  $\Delta_o$  can be measured easily using UV-Vis spec.

Example:  $[\text{Ti}(\text{OH}_2)_6]^{3+}$ , hexaaquatitanium(III) ion ( $\text{Ti}=d^1$ ).

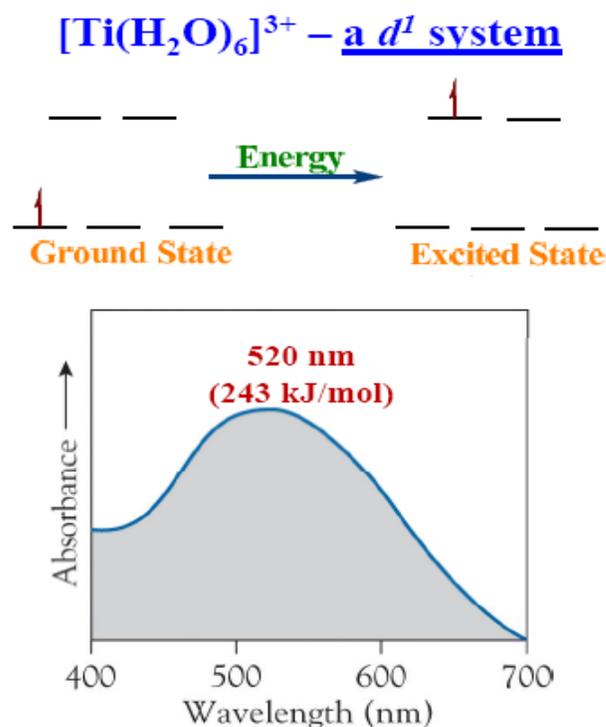
The complex absorbs light of the current wavelength (energy) to promote the electron from the  $t_{2g}$  level to the  $e_g$  level. ( $20300\text{cm}^{-1} = 493/520 \text{ nm}$ )

$$1\text{kJmol}^{-1} = 83.7\text{cm}^{-1}, \Delta_o = 20300/8.7 = 243\text{kJmol}^{-1}$$

The single  $d$  electron occupies an energy level  $2/5 \Delta_o$  which is below the average energy of the  $d$  orbitals because of the CFSE of the  $d$ -orbitals.

$$\text{CFSE} = 2/5 \times 243 = 97\text{kJmol}^{-1}$$

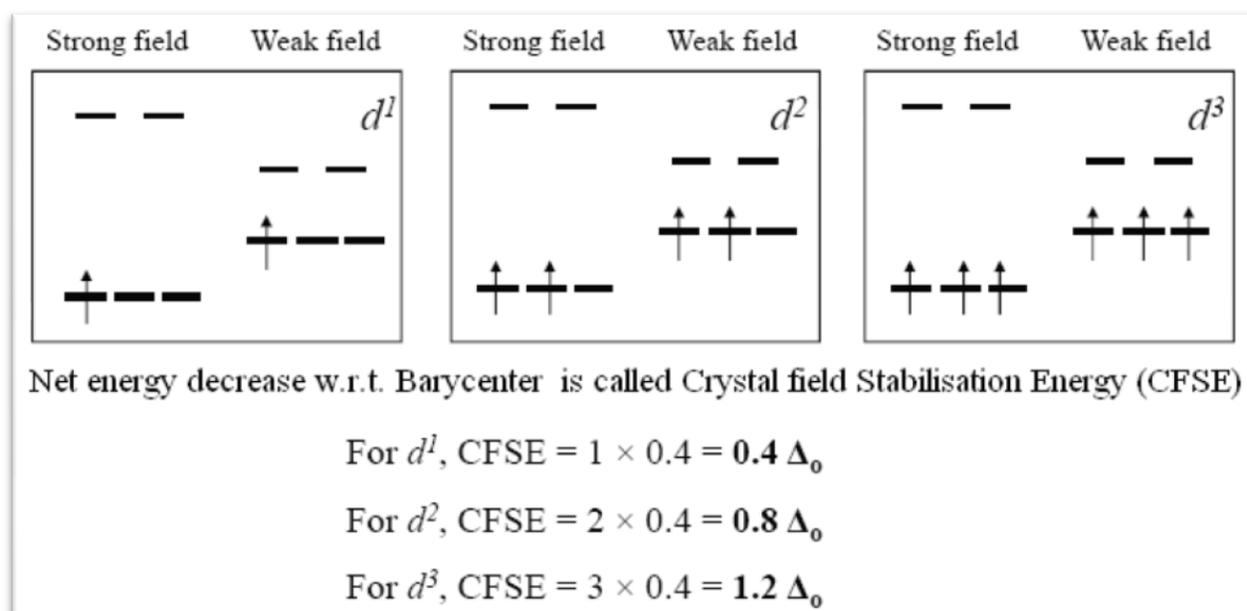
As a result the complex is stable



### CRYSTAL FIELD STABILIZATION ENERGY (CFSE)

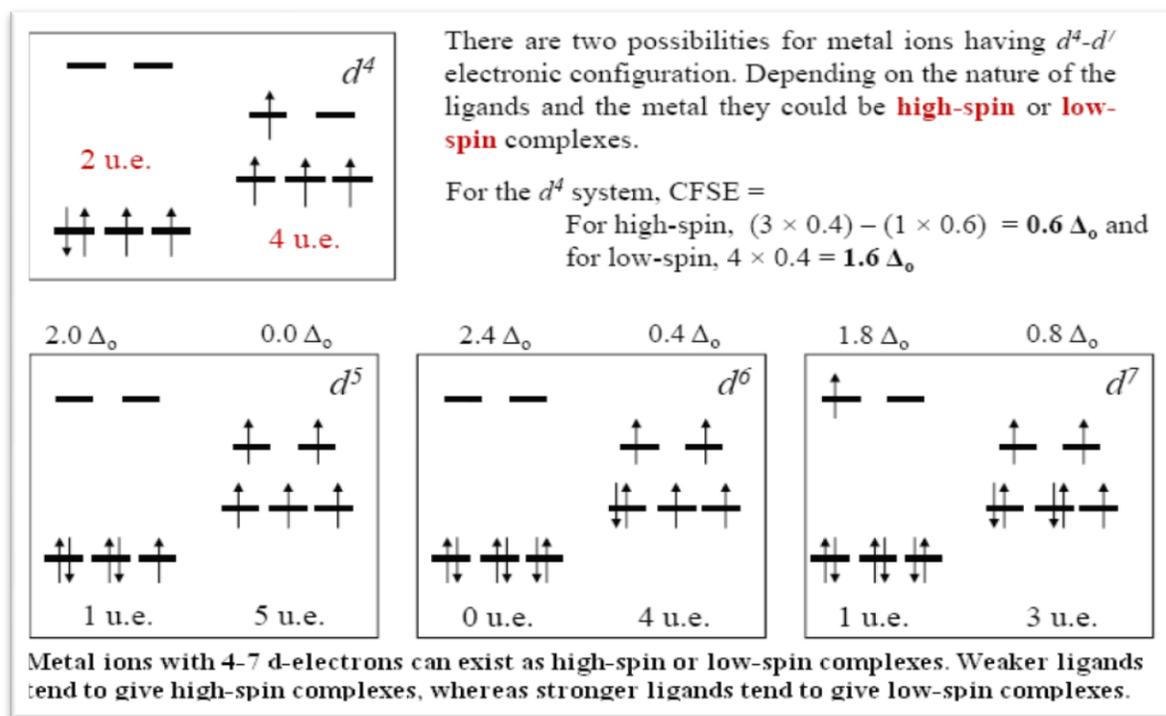
- The energy difference between the distribution of electrons in a particular crystal field and that for all electrons in the hypothetical spherical or uniform field levels is called the **crystal field stabilization energy** (CFSE) [This is the measure of the net energy of occupation of the  $d$  orbitals relative to their mean energy, Bary Centre].
- As we have seen, the energy difference between  $t_{2g}$  and  $e_g$  orbitals is defined as  $\Delta_o$ . The energy level of each of the two  $e_g$  orbitals would be  $0.6 \Delta_o$  above the zero of energy (barycenter), whereas the energy level of each of the three  $t_{2g}$  orbitals would be  $0.4 \Delta_o$  below the zero energy.

- Consider the example, the  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  ion.  $\text{Ti}^{3+}$  has a  $d^1$  electron configuration with the electron occupying  $t_{2g}$ , the crystal field stabilization energy (CFSE) is  $-0.4 \Delta_o$ . For  $d^2$ , the CFSE =  $-0.8 \Delta_o$  and for  $d^3$ , CFSE =  $-1.2 \Delta_o$ . Upon reaching the  $d^3$  configuration, however, the  $t_{2g}$  level becomes half-filled and there are no further orbitals of this energy to accept electrons without pairing.



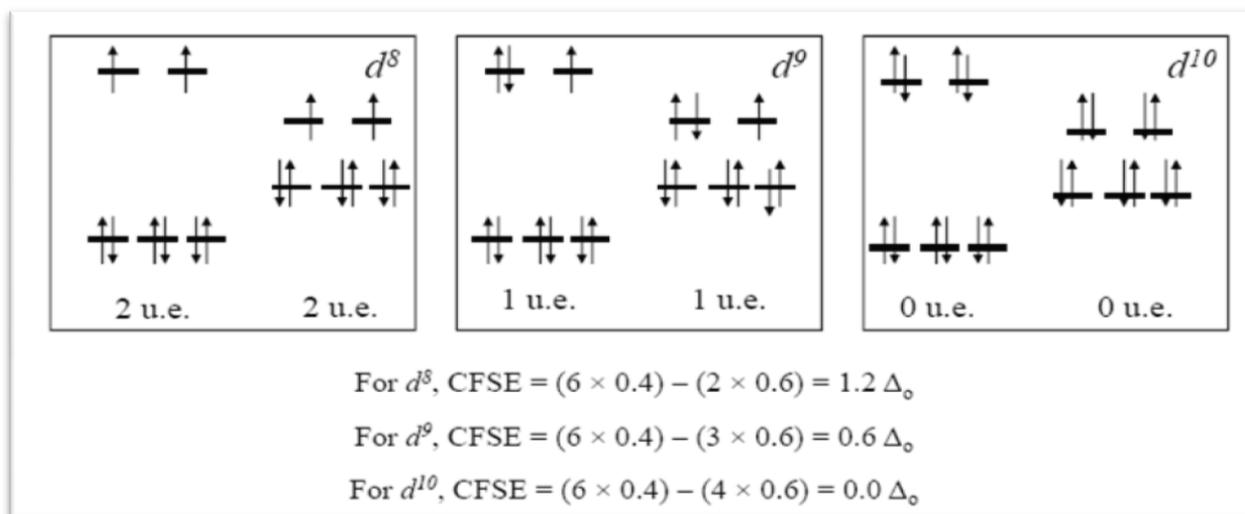
**Figure3: Distribution of electrons and CFSE for  $d^1$ - $d^3$  configurations**

- For configurations  $d^4$ ,  $d^5$ ,  $d^6$  and  $d^7$  two possibilities arise. The determining factor whether high-spin or low-spin complexes arise is the ligand-field splitting parameter. When  $\Delta_o$  is larger than the pairing energy  $P$  for the electrons, the electron pair in the  $t_{2g}$  orbitals as far as possible. If the energy required for pairing up the electrons (electrostatic repulsion) is greater than  $\Delta_o$ , the electrons will be distributed between  $t_{2g}$  and  $e_g$  levels. In the former case we have the strong-field ( $\Delta_o > P$ ) arrangement with low-spin complexes, while in the latter we have the weak-field ( $\Delta_o < P$ ) arrangement with high-spin complexes.



**Figure4: Distribution of electrons and CFSE for  $d^4$ - $d^7$  configurations**

- With  $d^8$ ,  $d^9$  and  $d^{10}$  configurations there is only one possible way for distributing the electrons between the  $t_{2g}$  and  $e_g$  orbitals.



**Figure4: Distribution of electrons and CFSE for  $d^4$ - $d^7$  configurations**

**Note:** In all the cases the electronic configuration involving two electrons in the same orbital, the actual CFSE is reduced by the energy spent on pairing the electrons

Table: Distribution of d-electrons in  $t_{2g}$  and  $e_g$  sets of orbitals of central metal ion surrounded by ligands in octahedral complexes.

No of electrons	Weak field ligand					CFSE	n	$s = \frac{n}{2}$	Strong field ligand					CFSE	n	$s = \frac{n}{2}$
	$t_{2g}$ orbitals			$e_g$ orbitals					$t_{2g}$ orbitals			$e_g$ orbitals				
$d^1(Ti^{3+})$	↑					$-4Dq$ or $-0.4\Delta_o$	1	$\frac{1}{2}$	↑					$-4Dq$ or $-0.4\Delta_o$	1	$\frac{1}{2}$
$d^2(Ti^{2+})$	↑	↑				$-8Dq$ or $-0.8\Delta_o$	2	1	↑	↑				$-8Dq$ or $-0.8\Delta_o$	2	1
$d^3(V^{2+})$	↑	↑	↑			$-12Dq$ or $-1.2\Delta_o$	3	$\frac{3}{2}$	↑	↑	↑			$-12Dq$ or $-1.2\Delta_o$	3	$\frac{3}{2}$
$d^4(Cr^{2+})$	↑	↑	↑	↑		$-6Dq$ or $-0.6\Delta_o$	4	2	↑↓	↑	↑			$-6Dq$ or $-0.6\Delta_o$	2	1
$d^5(Fe^{3+})$	↑	↑	↑	↑	↑	0	5	$\frac{5}{2}$	↑↓	↑↓	↑			0	1	$\frac{1}{2}$
$d^6(Co^{2+})$	↑↓	↑	↑	↑	↑	$-4Dq + P$ or $-0.4\Delta_o + P$	4	2	↑↓	↑↓	↑↓			$-4Dq + P$ or $-0.4\Delta_o + P$	0	0
$d^7(Co^{3+})$	↑↓	↑↓	↑	↑	↑	$-8Dq + 2P$ or $-0.8\Delta_o + 2P$	3	$\frac{3}{2}$	↑↓	↑↓	↑↓	↑		$-8Dq + 2P$ or $-0.8\Delta_o + 2P$	1	$\frac{1}{2}$
$d^8(Co^{2+})$	↑↓	↑↓	↑↓	↑	↑	$-12Dq + 3P$ or $-1.2\Delta_o + 3P$	2	1	↑↓	↑↓	↑↓	↑	↑	$-12Dq + 3P$ or $-1.2\Delta_o + 3P$	2	1
$d^9(Cu^{2+})$	↑↓	↑↓	↑↓	↑↓	↑	$-6Dq + 4P$ or $-0.6\Delta_o + 4P$	1	$\frac{1}{2}$	↑↓	↑↓	↑↓	↑↓	↑	$-6Dq + 4P$ or $-0.6\Delta_o + 4P$	1	$\frac{1}{2}$
$d^{10}(Zn^{2+})$	↑↓	↑↓	↑↓	↑↓	↑↓	$0Dq + 5P$	0	0	↑↓	↑↓	↑↓	↑↓	↑↓	$0Dq + 5P$	0	0

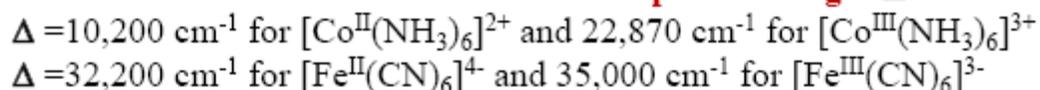
 Table1: Octahedral crystal field stabilization energies (CFSE) for  $d^n$  configurations.

## THE FACTORS AFFECTING CRYSTAL FIELD SPLITTING ENERGY, $\Delta$ OR $10Dq$

- There are several factors that affect the extent of splitting of the d-orbitals by ligands.

(I) **Oxidation state of the metal** . For a given metal, the change of the oxidation state from +2 to +3 would result in a corresponding increase in  $\Delta$  by 50% . The increased charge of the metal ion will draw the ligands in more closely, hence they will have a greater effect in perturbing the metal d-orbitals.

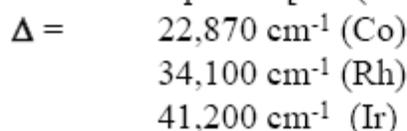
**Higher oxidation states of the metal atom correspond to larger  $\Delta$ .**



(II) **Nature of the metal ion involved** . For a given transition series the differences are not great, but within a given group in progressing from 3d  $\rightarrow$  4d  $\rightarrow$  5d the value of  $\Delta$  increases by 25 - 50%.

**In groups, heavier analogues have larger  $\Delta$ .**

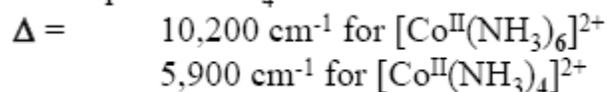
For hexaammine complexes  $[\text{M}^{\text{III}}(\text{NH}_3)_6]^{3+}$ :



(III) **Geometry of the complex** . The splitting in an octahedral field is about twice as strong as for a tetrahedral field for the same metal ion and the same ligands . In tetrahedral complex the ligands are directed much less efficiently than in octahedral complex

**Geometry of the metal coordination unit affects  $\Delta$  greatly.**

Tetrahedral complexes  $\text{ML}_4$  have smaller  $\Delta$  than octahedral ones  $\text{ML}_6$ :



(IV) **Nature and Number of the ligands** . Different ligands cause different degree of splitting.

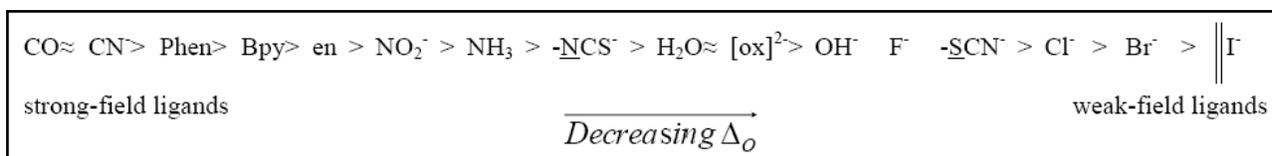
**Nature of the ligands.**

For  $[\text{Co}^{\text{III}}\text{L}_6]$ ,  $\Delta$  in  $\text{cm}^{-1}$ : 13,100 ( $\text{F}^-$ ); 20,760 ( $\text{H}_2\text{O}$ ); 22,870 ( $\text{NH}_3$ )

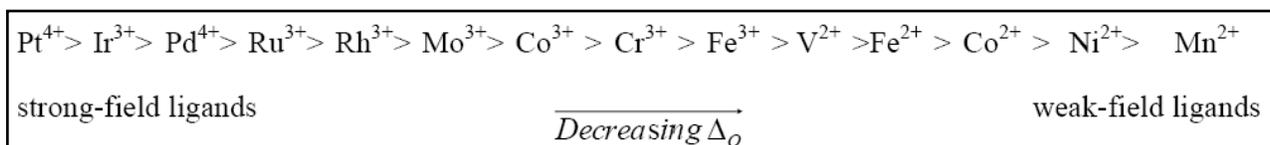
For  $[\text{Cr}^{\text{III}}\text{L}_6]$ ,  $\Delta$  in  $\text{cm}^{-1}$ : 15,060 ( $\text{F}^-$ ); 17,400 ( $\text{H}_2\text{O}$ ); 26,600 ( $\text{CN}^-$ )

- Depending on the charge (or oxidation state) and nature of metal ion (or metal) and ligand, the strength of the crystal field may be varied from strong to weak.  
 $\Delta$  (strong field) >  $\Delta$  (weak field)
- It is possible to list ligands or metal ions in order of increasing field strength in a " spectrochemical series " .

i) Spectrochemical series for ligands



ii) Spectrochemical series for metal ions



*The value of  $\Delta_o$  increases with increasing oxidation number of the central metal ion. The variation of oxidation number reflects the smaller size of more highly charged ions and consequently shorter metal-ligand distances and stronger interaction energies. The value of  $\Delta_o$  increases down the group. This reflects the larger size of the 4d and 5d orbitals compared with the compact 3d orbitals and the consequent stronger interaction of the ligands.*

### Problems

#### 1. Calculate CFSE for the complex $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$

Chromium in ground state is  $[\text{Ar}]3d^5 4s^1$ , in +2 state, will be a  $d^4$  system with  $t_{2g}^3 e_g^1$  configuration of electrons because  $\text{H}_2\text{O}$  is a weak field ligand. CFSE will be therefore

$$-0.4 \Delta_0 \times 3 + 0.6 \Delta_0 = -0.6 \Delta_0$$

#### 2. Calculate CFSE for $[\text{Fe}(\text{CN})_6]^{4-}$

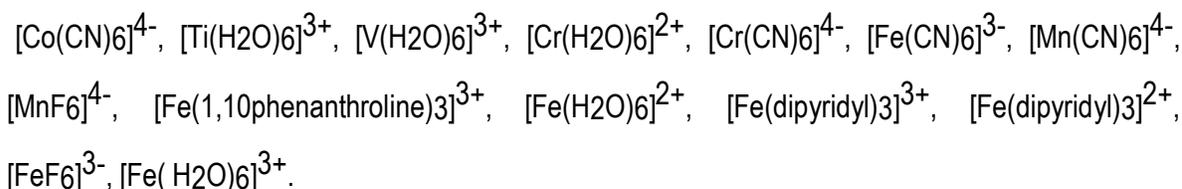
Iron in ground state is  $[\text{Ar}]3d^6 4s^2$ , in +2 state it will be a  $d^6$  system with  $t_{2g}^6 e_g^0$  configuration of electrons because  $\text{CN}^-$  is a strong field ligand. Therefore, CFSE be

$$-0.4 \Delta_0 \times 6 + 2P = -2.4 \Delta_0 + 2P$$

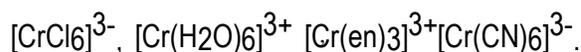
### Exercise for Practice

1. An aqueous solution of titanium chloride shows zero magnetic moment. Write down its formula assuming it to be an octahedral complex in aqueous solution.

2. Calculate CFSE for the following complexes-



3. Give correct order for the energy gap between two sets of d orbitals in the following complexes-



4. Give correct order for energy gap between two sets of d levels in the following complexes –

