



# WILSON COLLEGE, MUMBAI

DEPARTMENT OF CHEMISTRY

UNDERGRADUATE SEMESTER -VI

INORGANIC CHEMISTRY

MODULE III

TOPIC: THEORIES OF THE METAL - LIGAND BOND

DR SAKINA.Z. BOOTWALA

HEAD OF DEPARTMENT

<b>SUBJECT</b>	<b>CHEMISTRY</b>
<b>Paper No and Title</b>	Inorganic Chemistry –II
<b>Module No</b>	Module- III
<b>Title</b>	MEASUREMENT & FACTORS AFFECTING MAGNITUDE OF $10Dq$

## **TABLE OF CONTENTS**

1. LEARNING OUTCOMES
2. MEASUREMENT OF  $10Dq$
3. FACTORS AFFECTING MAGNITUDE OF  $10Dq$
4. SPECTROCHEMICAL SERIES
5. WORKSHEET
6. SUMMARY

## LEARNING OUTCOMES

- Learners will know how to calculate  $10Dq$  from the spectra
- From the  $10Dq$  value they will learn to calculate crystal field stabilisation energies of various complexes.
- Learners will also understand factors affecting  $10Dq$  values
- Learners will the position of ligands in spectrochemical series and hence identify weak and strong ligands

## MEASUREMENT OF $10Dq$ :

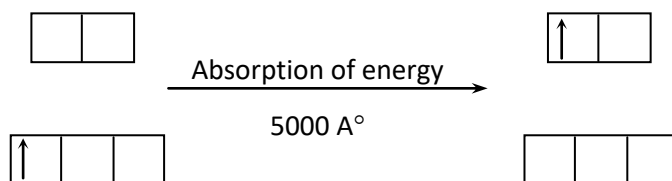
1. The term  $Dq$  is the product of two terms  $D$  and  $q$  and is called Differential of quanta implying the energy .The energy gap  $10Dq$  between the  $t_{2g}$  and  $e_g$  orbitals can be determined from the absorption spectrum of the complex.
2. The excitation of electrons, from the lower energy orbitals to the higher energy orbitals is achieved by the absorption of low energy radiations present in the visible light.
3. If  $\lambda$  is the wavelength of the radiation absorbed, the energy associated with it is given by the relationship:  $E = hc / \lambda$  where  $h$  is Planck's constant and  $c$  is velocity of light. From the value of  $E$ ,  $10Dq$  can be determined.

Determine the value of  $10Dq$  of the complex ion,  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ . The absorption spectrum of

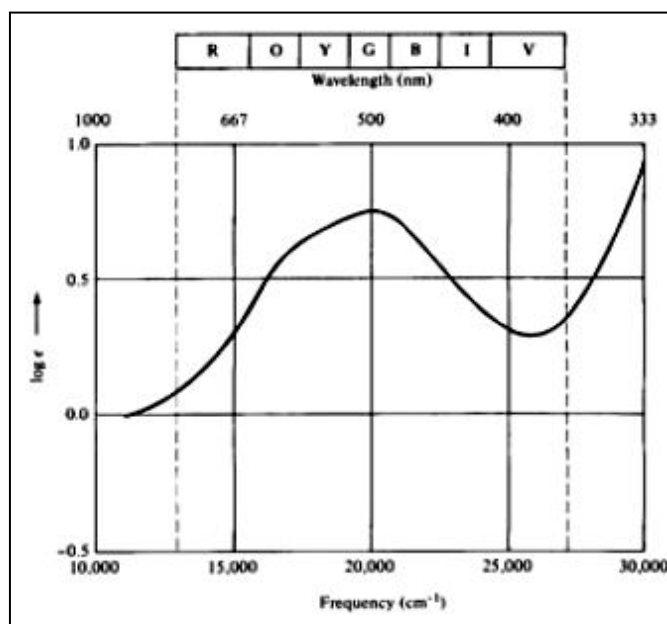
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is shown

- $\text{Ti}^{3+}$  ion has  $d^1$  electron configuration, hence the  $d^1$  electron will occupy one of the lower degenerate  $t_{2g}$  orbitals.
- When the complex absorbs light of proper wavelength, the electron from  $t_{2g}$  orbital (ground state) will be promoted to the  $e_g$  orbital (excited state).

- Since the transition of electron takes place from one set of *d* orbitals to another set of *d* orbitals, it is called *d-d* transition and the observed and absorption band in the spectrum is called *d-d* transition band.
- From the frequency of *d-d* transition band, value of  $10Dq$  can be calculated.



Ground State electronic configuration      Excited State electronic configuration



- It is clear from the spectrum that there is only one absorption maxima at a frequency  $(\lambda = 500 \text{ nm})$ . The frequency of  $2.03 \times 10^6 \text{ m}^{-1}$   $[(1/\lambda) \times 10^9]$   $(\text{nm} = 1 \times 10^{-9} \text{ m})$

$$E = h\nu = h\tilde{\nu}c$$

$$E = 6.626 \times 10^{-34} \text{ J molecule}^{-1} \times 2.0 \times 10^6 \text{ m}^{-1} \times 3 \times 10^8 \text{ ms}^{-1}$$

$$E = 3.975 \times 10^{-19} \text{ J molecule}^{-1}$$

$$E = 3.975 \times 10^{-19} \text{ J molecule}^{-1} \times 6.023 \times 10^{23} \text{ molecules mole}^{-1}$$

$$E = 239.4 \times 10^3 \text{ Joules mole}^{-1} = 239.4 \text{ KJ mol}^{-1}$$

$$\text{Thus } 10Dq = 239.4 \text{ KJ mol}^{-1} = 57.20 \text{ Kcal mol}^{-1} \quad (1 \text{ KJ mol}^{-1} = 0.2390 \text{ Kcal mol}^{-1})$$

$$Dq = 23.94 \text{ KJ mol}^{-1}$$

$$\text{CFSE for } d^1 \text{ electronic configuration is } = -4Dq = -4 \times 23.94 = -95.76 \text{ KJ mol}^{-1}$$

- A solution containing  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is violet in colour because it absorbs **green & yellow** light in the region of 500 nm wavelength and hence the transmitted light is only a mixture of **blue & red**.
- Thus on the basis of CFT, spectral properties of complexes can be explained.

### **Factors Affecting Magnitude of 10Dq :**

The extent of splitting of d orbitals, i.e. the magnitude of 10Dq is influenced by a number of factors like :

- A) Geometry of the complex, B) Nature of the ligands, C) Charge on the metal ion, and  
D) Position of the metal in the transition series, i.e. whether it is in the 1<sup>st</sup>, 2<sup>nd</sup> or 3<sup>rd</sup> transition series.

#### **A. Geometry of the complex :**

In octahedral complexes, the splitting of *d* orbitals is more than **twice** as strong as in tetrahedral complexes for the same metal ion and ligands. This difference in 10Dq value is because of two factors :

- i) In octahedral complexes **six ligands** are involved while in tetrahedral **only four**; this results in 33 % decrease in the field strength, provided the other factors remain the same.
- ii) In octahedral complexes, the ligands are situated **exactly in the direction** of  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals while in tetrahedral complexes the

ligands are not aimed at any of the d orbitals but exert more influence on the  $t_{2g}$  orbitals than on the  $e_g$  orbitals. In case of square planar complexes, the degree of splitting is more than in a tetrahedral field.

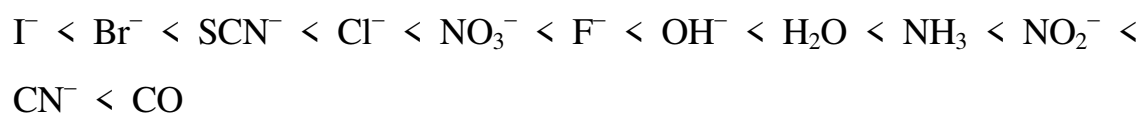
### B. Nature of the ligands :

By examining the absorption spectra of various transition metal complexes, it has been found that the position of absorption spectra and hence the value of  $10Dq$  for any given metal ion depends upon the ligands attached to it. The values of  $10Dq$  for a number of  $Cr^{3+}$  complexes with different ligands are given below :

#### Crystal field splitting by various ligands

Complex	Absorption peak $m^{-1}$	$10Dq$ or $kJ.mol^{-1}$
$[CrCl_6]^{3-}$	13,64000	163.27
$[Cr(H_2O)_6]^{3+}$	17,83000	213.4
$[Cr(NH_3)_6]^{3+}$	21,68000	259.5
$[Cr(CN)_6]^{3-}$	26,28000	314.6

Cyanide ligand produces more splitting and hence is a strong ligand. Chloride ligand produces less splitting and is a weak ligand. The common ligands can be arranged in the order of their strength, in the form of a series called **SPECTROCHEMICAL SERIES**.



### C. Charge on the metal ion :

Since crystal field theory is based on the electrostatic model, the ionic charge on the central metal has a direct effect on the magnitude of  $10Dq$ . In

general a metal ion with higher charge draws the ligands more closely, and hence produces more splitting than cation with lower charge. Thus  $10Dq$  values of hexaquo complexes of  $Cr^{2+}$  and  $Cr^{3+}$  are  $166.1 \text{ KJ.mol}^{-1}$  and  $213.1 \text{ KJ.mol}^{-1}$  respectively.

**D. Position of the metal in the transition series (1<sup>st</sup> / 2<sup>nd</sup> / 3<sup>rd</sup> series) :**

The extent of crystal field splitting varies with the metal of the first transition series to the metal of third transition series, involving 3d, and 5d orbitals respectively. In general, the value of  $10Dq$  increases on descending a group of transition elements, i.e. from first to third transition series.

Crystal field splitting in one group of elements

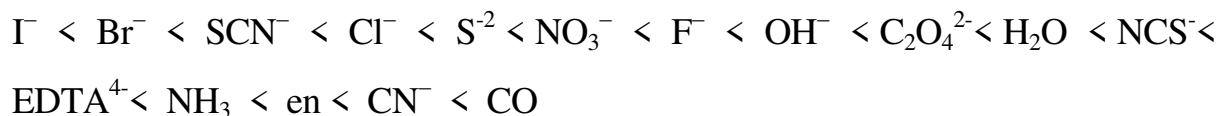
Transition series	Complex	'd' electrons in	$\text{cm}^{-1}$	$\Delta_0$ $\text{kJ.mol}^{-1}$
I	$[Co(NH_3)_6]^{3+}$	3d	23,00000	274.9
II	$[Rh(NH_3)_6]^{3+}$	4d	34,00000	406.4
II	$[Ir(NH_3)_6]^{3+}$	5d	41,00000	489.9

**SPECTROCHEMICAL SERIES :**

- One of the factors which affect the degree of splitting of d orbitals in complexes is the nature of the ligands.
- The magnitude of splitting energy  $\Delta_0$  depends upon the splitting power of ligands.
- The value of  $\Delta_0$  can be equated to the energy observed as the maximum in the absorption spectra of complexes as explained for  $[Ti(H_2O)_6]^{3+}$ .
- For example, from the absorption spectra of  $Co^{3+}$  and  $Cr^{3+}$  complexes. It is clear that the splitting power on ligand field strength of the three ligands is

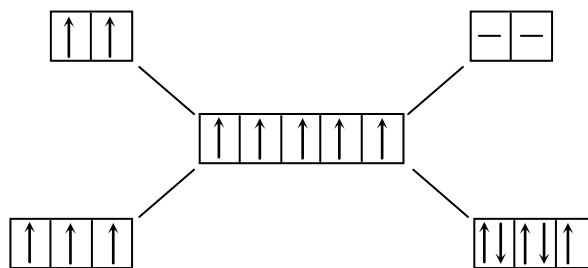


in the order  $\text{CN}^- > \text{NH}_3 > \text{H}_2\text{O}$ . Depending upon their field strength, the common ligands are arranged in the form of a series i.e.



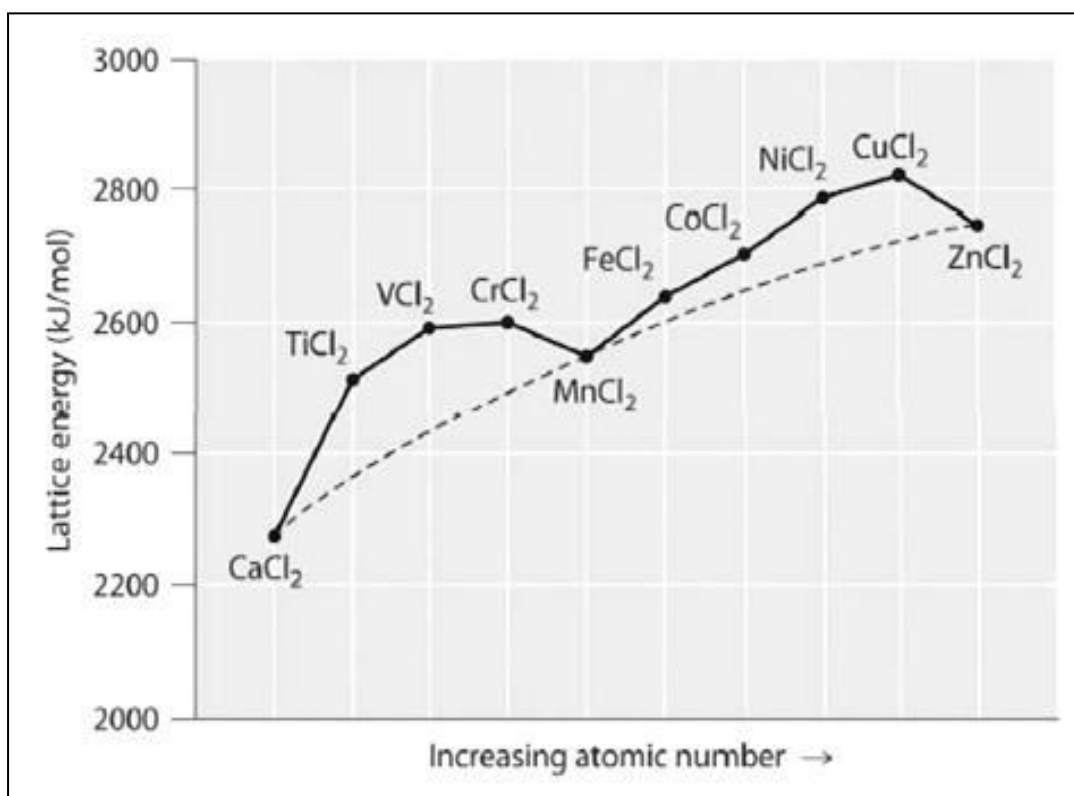
This arrangement of ligands in the order of increasing field strength is called **Fajans–Tschida Spectrochemical Series** because it is derived from spectral studies of the complexes.

- The ligands on the right side of the series provide the strongest field (high  $\Delta_0$ ) and are the most effective in forcing the cations into low spin states,
- Whereas the ligands on the left, provide weak field (low  $\Delta_0$ ) and usually give high spin complexes.
- Formation of two octahedral complexes of  $\text{Fe}^{3+}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  can explain the effect of weak ligand field and strong ligand field, where  $\text{Fe}^{3+}$  has  $d^5$  configuration.
- Since  $\text{H}_2\text{O}$  is a weaker ligand than  $\text{CN}^-$  ion, the value of splitting energy ( $\Delta_0$ ) is smaller in  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  than in  $(\text{Fe}(\text{CN})_6)^{3-}$ . Hence, the five d electrons of  $\text{Fe}^{3+}$  will occupy all the  $t_{2g}$  and  $e_g$  levels without pairing, resulting in a high spin complex with 5 unpaired electrons. Thus  $(\text{Fe}(\text{H}_2\text{O})_6)^{3+}$  is a highly paramagnetic complex. In case of  $[\text{Fe}(\text{CN})_6]^{3-}$  the value of  $\Delta_0$  is sufficiently high to force pairing of  $t_{2g}$  electrons. Thus in  $[\text{Fe}(\text{CN})_6]^{3-}$  there are two pairs of electrons in two  $t_{2g}$  orbitals. Hence it is also paramagnetic in nature but it is less paramagnetic as compared to  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ .



High Spin Complex =  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$     Low Spin Complex =  $[\text{Fe}(\text{CN})_6]^{3-}$

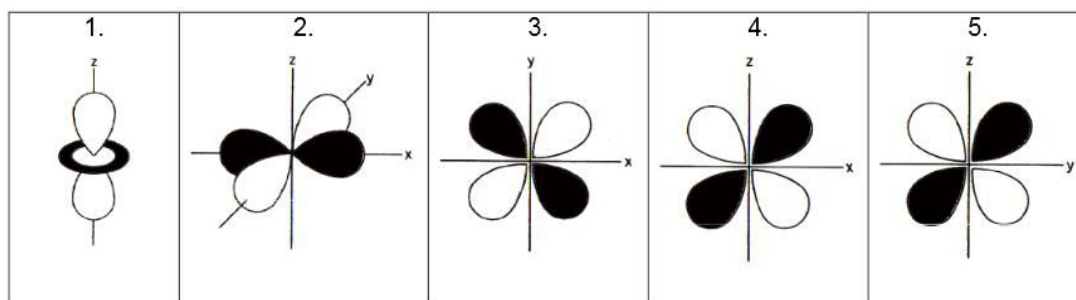
- The others with  $d^2, d^4, d^7$  and  $d^8$  configurations show less variation as they show comparatively less CFSE. Thus, the double humped curve and the variation in lattice energies are explained by crystal field splitting.



## WORKSHEET

### 1: The d-Orbitals

It is necessary to know the d-orbitals by name for this discussion. Below each of these orbitals identify their name (i.e.,  $d_{xy}$ ,  $d_{x^2-y^2}$ ,  $d_{zy}$ ,  $d_{z^2}$ ,  $d_{xy}$ ). Pay careful attention to the axis plotted.



### 2: The Ligand Field

Now consider an octahedron complex  $ML_6^m$ , where  $m$  is the charge on complex and  $L$  is a monodentate ligand (e.g., the chloro- ligand). sketch an octahedral "ligand field" in 3D with six black balls to represent the six ligands. Place one "ligand ball" on one of the axes (e.g.,  $-x$ ,  $x$ ,  $-y$ ,  $y$ ,  $z$  and  $-z$ ). You do not need to draw the transition metal, since the five d-orbitals are attributed to it.

### **3: The Energy Diagram in Absence of Ligand Field**

Draw the energies of the five d orbitals in five energetically horizontal lines to represent that they are degenerate (same energy). Draw those five horizontal lines to represent the energies of the d-orbitals in the absence of the ligand field.

### **4: The Energy Diagram in Presence of Octahedral Ligand Field**

### **5: Energy Splitting**

## 6: Draw the Energy Diagram for $Ti^{+3}$

### 7: Low Spin vs. High Spin Configurations

When the electrons choose to occupy the higher energy orbitals rather than pairing up, the situation is called *high-spin* because the number of unpaired electron is maximized. When they pair up, the situation is called *low-spin*. High/low-spin possibilities only occur for a few d-electron configurations. What are they?

## 8: The Full Row

Complete the following table for octahedral metal ions in an octahedral crystal field. For each situation, sketch the energy splitting pattern, fill the orbitals, determine the total CFSE stabilization and the number of unpaired electrons. For electron configurations such as  $d^1d^1$ , where high/low spin is not an option, just show your work in the “high-spin” columns in the table and leave the low spin columns blank.

	High Spin			Low Spin		
	Energy diagram	CFSE	Number unpaired electrons	Energy diagram	CFSE	Number unpaired electrons
$d^0$						
$d^1$						
$d^2$						
$d^3$						
$d^4$						
$d^5$						
$d^6$						
$d^7$						
$d^8$						
$d^9$						
$d^{10}$						

9 Which these compounds is paramagnetic (unpaired electrons present)?

- a.  $K_3[FeCl_6]$
- b.  $KMnO_4$
- c.  $ZnSO_4$
- d.  $TiCl_4$

10. The number of unpaired electrons in  $K_4[Co(CN)_6]$  is

- a. 0
- b. 1
- c. 2
- d. 3
- e. None of these

11. Which compound is diamagnetic (all electron paired)?

- a.  $K_4[Co(CN)_6]$
- b.  $[Cr(NH_3)_6]SO_4$
- c.  $[Mn(H_2O)_6](Cl)_2$
- d.  $K_2[ZnCl_4]$
- e.  $K_3[FeCl_6]K_3[FeCl_6]$

12. Which would have the largest value of  $\Delta_o$ ?

- a.  $[Fe(CN)_6]^{-3}$
- b.  $[Fe(CN)_6]^{-4}$
- c.  $[Co(NH_3)_6]^{+2}$
- d.  $[Ni(NH_3)_4]^{+2}$
- e.  $[Co(NH_3)_3(Cl)_3]$

13 Which would have the largest crystal field stabilization energy?

- a. octahedral complex with d<sup>3</sup> configuration
- b. octahedral complex with d<sup>4</sup> low spin configuration
- c. tetrahedral complex with d<sup>5</sup> configuration

14. In which of compounds is the one most likely to be high spin listed first?

- a. [Ru(H<sub>2</sub>O)<sub>6</sub>]<sup>+3</sup> and [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>+3</sup>
- b. [Mn(Cl)<sub>6</sub>]<sup>-3</sup> and [Mn(Cl)<sub>6</sub>]<sup>-4</sup>
- c. [Fe(Cl)<sub>6</sub>]<sup>-3</sup> and [Fe(Cl)<sub>4</sub>]<sup>-</sup>
- d. [Ni(NH<sub>3</sub>)<sub>4</sub>]<sup>+2</sup> and [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>+2</sup>
- e. [Fe(CN)<sub>6</sub>]<sup>-3</sup> and [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>+3</sup>

15. Which is not a factor when predicting  $\Delta_o$ ?

- a. oxidation state of metal
- b. Spectrochemical series
- c. whether the metal is from n = 3, 4 or 5.
- d. the geometry of the complex.
- e. the charge on the ligand



## SUMMARY:

- Calculation  $10Dq$  from the spectra
- Calculate crystal field stabilisation energies of various complexes.
- Factors affecting  $10Dq$  values
- Position of ligands in spectrochemical series .