<table>
<thead>
<tr>
<th>SUBJECT</th>
<th>CHEMISTRY</th>
</tr>
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<tbody>
<tr>
<td>Paper No and Title</td>
<td>Inorganic Chemistry –II</td>
</tr>
<tr>
<td>Module No</td>
<td>Module- III</td>
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<td>MEASUREMENT &amp; FACTORS AFFECTING MAGNITUDE OF 10Dq</td>
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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: \( E = \frac{hc}{\lambda} \) 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, [Ti (H_2O)_6]^{3+}. The absorption spectrum of [Ti (H_2O)_6]^{3+} is shown

- 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.

\[
\text{Ground State electronic configuration} \quad \text{Excited State electronic configuration}
\]

\[
\text{Absorption of energy} \quad 5000 \, \text{Å} \quad \text{Ground State electronic configuration} \quad \text{Excited State electronic configuration}
\]

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

\[
\left(\frac{1}{\lambda}\right) \times 10^9 \quad (\text{nm}=1 \times 10^{-9} \, \text{m})
\]

\[
E = \hbar \nu = h \frac{\nu}{c}
\]

\[
E = 6.626 \times 10^{-34} \, \text{J} \, \text{molecule}^{-1} \times 2.0 \times 10^6 \, \text{m}^{-1} \times 3 \times 10^8 \, \text{m} \cdot \text{s}^{-1}
\]

\[
E = 3.975 \times 10^{-19} \, \text{J} \, \text{molecule}^{-1}
\]

\[
E = 3.975 \times 10^{-19} \, \text{J} \, \text{molecule}^{-1} \times 6.023 \times 10^{23} \, \text{molecules mole}^{-1}
\]
E= 239.4 × 10^3 Joules mole\(^{-1}\) = 239.4 KL mol\(^{-1}\)
Thus 10Dq= 239.4 KJ mol\(^{-1}\) = 57.20 Kcal mol\(^{-1}\)  
(1 KJ mol\(^{-1}\) = 0.2390 Kcal mol\(^{-1}\))
Dq=23.94 KJ mol\(^{-1}\)
CFSE for d\(^1\) electronic configuration is = -4Dq= -4× 23.94= -95.76 KJ mol\(^{-1}\)

- A solution containing [Ti (H\(_2\)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\(^{st}\), 2\(^{nd}\) or 3\(^{rd}\) 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\(_{x^2}\) 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

<table>
<thead>
<tr>
<th>Complex</th>
<th>Absorption peak m(^{-1} )</th>
<th>10Dq or ( kj.mol^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{CrCl}_6]^{3-})</td>
<td>13.640000</td>
<td>163.27</td>
</tr>
<tr>
<td>([\text{Cr(H}_2\text{O)}_6]^{3+})</td>
<td>17.83000</td>
<td>213.4</td>
</tr>
<tr>
<td>([\text{Cr(NH}_3)_6]^{3+})</td>
<td>21.68000</td>
<td>259.5</td>
</tr>
<tr>
<td>([\text{Cr(CN)}_6]^{3-})</td>
<td>26.28000</td>
<td>314.6</td>
</tr>
</tbody>
</table>

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**.

\( \Gamma^- < \text{Br}^- < \text{SCN}^- < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{NO}_2^- < \text{CN}^- < \text{CO} \)

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 hexaaquo complexes of Cr\textsuperscript{2+} and Cr\textsuperscript{3+} are 166.1 KJ.mol\textsuperscript{-1} and 213.1 KJ.mol\textsuperscript{-1} respectively.

D. **Position of the metal in the transition series (1\textsuperscript{st} / 2\textsuperscript{nd} / 3\textsuperscript{rd} series)**:

The extent of crystal field splitting various 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**

<table>
<thead>
<tr>
<th>Transition series</th>
<th>Complex</th>
<th>‘d’ electrons in</th>
<th>(\Delta_0) cm\textsuperscript{-1}</th>
<th>(\Delta_0) kJ.mol\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>[Co(NH\textsubscript{3})\textsubscript{6}]\textsuperscript{3+}</td>
<td>3d</td>
<td>23,00000</td>
<td>274.9</td>
</tr>
<tr>
<td>II</td>
<td>[Rh(NH\textsubscript{3})\textsubscript{6}]\textsuperscript{3+}</td>
<td>4d</td>
<td>34,00000</td>
<td>406.4</td>
</tr>
<tr>
<td>II</td>
<td>[Ir(NH\textsubscript{3})\textsubscript{6}]\textsuperscript{3+}</td>
<td>5d</td>
<td>41,00000</td>
<td>489.9</td>
</tr>
</tbody>
</table>

**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 \[Ti (H\textsubscript{2}O)\textsubscript{6}\]\textsuperscript{3+}.
- For example, from the absorption spectra of Co\textsuperscript{3+} and Cr\textsuperscript{3+} complexes. It is clear that the splitting power on ligand field strength of the three ligands is...
in the order CN\(^-\) > NH\(_3\) > H\(_2\)O. Depending upon their field strength, the common ligands are arranged in the form of a series i.e.
\[\Gamma^- < Br^- < SCN^- < Cl^- < S^2^- < NO_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO\]

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 Fe\(^{3+}\), \([Fe(H_2O)_6]^{3+}\) and \([Fe(CN)_6]^{3-}\) can explain the effect of weak ligand field and strong ligand field, where Fe\(^{3+}\) has \(d^5\) configuration.
- Since H\(_2\)O is a weaker ligand than CN\(^-\) ion, the value of splitting energy (\(\Delta_0\)) is smaller in \([Fe(H_2O)_6]^{3+}\) than in \([Fe(CN)_6]^{3-}\). Hence, the five d electrons of 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 \([Fe(H_2O)_6]^{3+}\) is a highly paramagnetic complex. In case of \([Fe(CN)_6]^{3-}\) the value of \(\Delta_0\) is sufficiently high to force pairing of \(t_{2g}\) electrons. Thus in \([Fe(CN)_6]^{3-}\) 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 \([Fe(H_2O)_6]^{3+}\).
High Spin Complex = $[\text{Fe(H}_2\text{O)}_6]^{3-}$  
Low Spin Complex = $[\text{Fe(CN)}_6]^{3-}$

- 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 know the d-orbitals by name for this discussion. Below each of the these orbitals identify their name (i.e., dxy, dx2-y2, dzy, dz2,dxy,). Pay careful attention to the axis plotted.

2: The Ligand Field

Now consider an octahedron complex  ML6m, where mm is the charge on complex and L is a monodentate ligand (e.g., the chloro- ligand). sketch an octahedral "ligand field" in3D 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 CSFE stabilization and the number of unpaired electrons. For electron configurations such as d1d1, 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.

<table>
<thead>
<tr>
<th></th>
<th>High Spin</th>
<th>Low Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Energy diagram</td>
<td>CFSE</td>
</tr>
<tr>
<td>d⁰</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d⁴</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d⁵</td>
<td></td>
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<tr>
<td>d⁶</td>
<td></td>
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<tr>
<td>d⁷</td>
<td></td>
<td></td>
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<tr>
<td>d⁸</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d⁹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d¹⁰</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
9 Which of these compounds is paramagnetic (unpaired electrons present)?

- a. K3[FeCl6]
- b. KMnO4
- c. ZnSO4
- d. TiCl4

10. The number of unpaired electrons in K4[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. K4[Co(CN)6]
- b. [Cr(NH3)6]SO4
- c. [Mn(H2O)6](Cl)2
- d. K2[ZnCl4]

12. Which would have the largest value of Δ₀?

- a. [Fe(CN)₆]⁻³
- b. [Fe(CN)₆]⁻⁴
- c. [Co(NH₃)₆]⁺²
- d. [Ni(NH₃)₄]⁺²
- e. [Co(NH₃)₃(Cl)₃]
13. Which would have the largest crystal field stabilization energy?
   a. octahedral complex with d3 configuration
   b. octahedral complex with d4 low spin configuration
   c. tetrahedral complex with d5 configuration

14. In which of compounds is the one most likely to be high spin listed first?
   a. [Ru(H2O)6]+3 and [Fe(H2O)6]+3
   b. [Mn(Cl)6]−3 and [Mn(Cl)6]−4
   c. [Fe(Cl)6]−3 and [Fe(Cl)4]−
   d. [Ni(NH3)4]+2 and [Pt(NH3)4]+2
   e. [Fe(CN)6]−3 and [Fe(H2O)6]+3

15. Which is not a factor when predicting ΔoΔo?
   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 of 10Dq from the spectra
- Calculate crystal field stabilisation energies of various complexes.
- Factors affecting 10Dq values
- Position of ligands in spectrochemical series.