M.Sc. Semester-II, Paper: CC-06 (Inorganic Chemistry)

Unit-1 Electronic spectra of transition metal complexes [By Dr. Birendra Kumar, Maharaja college]

## Tanabe-Sugano diagram:

Tanabe-Sugano diagram is used in coordination Chemistry to predict absorptions in the UV, Visible and IR electromagnetic spectrum of coordination compounds. The results from a Tanabe-Sugano diagram analysis of a metal complex can also be compared to experimental Spectroscopic data. They can also be used to predict the size of the ligand field necessary to cause high spin to low spin transitions. In a Tanabe-Sugano diagram, the ground state is used as a constant reference, in contrast to Orgel diagram. They show both spin allowed and spin-forbidden transitions. They also show both high spin and low spin complexes.

In Tanabe-Sugano diagram, the ground state is always taken as the abscissa (horizontal axis) which provides a constant reference point. The other energy states are plotted relative to this ground state. The energy of transition of electron from the ground to the excited states can be calculated by the vertical distance from the ground state. In order to make the diagram general for different metal ions with the same electronic configurations and to acknowledge for different ligands, both of which affect $D_q$ and B or B', the axes are plotted in units of energy/B (i.e; E/B) and $D_q/B$. for examples, $d^5$ diagram equally applies for the both $Mn^{2+}(d^5)$ & $Fe^{3+}(d^5)$ where for each metal ion the corresponding value of B is used.

Left hand Ordinate represents the energies of the Russell-Saunders terms of the free ion in units of B (E/B). Abscissa represents the crystal field strength $10D_q$ in units of B ($D_q/B$). The energies of states with spin multiplicity different from those of the ground states are also included in this diagram. Configuration interaction is included as bending of lines for the excited states. These states require Racah parameters B & C (inter electronic repulsion parameters) in the analytical expressions for their energies. Thus, State energies in Tanabe-Sugano diagrams are dependent on $D_q$, B' & C' and thus would need a four dimensional plot. It can be simplified by assuming that $C' = 4.5B'$ and to express both the state energies and $D_q$ as multiples of B'. The value of B & C are different for different metal ions and are characteristics of a metal ion.

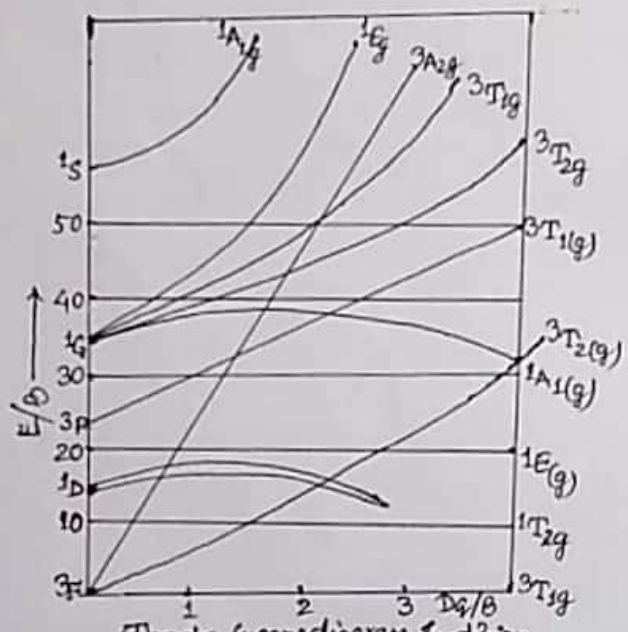
Hence, the ordinate is taken in units of E/B' and the abscissa is in units of $D_q/B'$. The position of the spectral states are function of two parameters $D_q$ & B.

The simple relation $C' = 4.5B'$ may not be true in every case, so Tanabe-Sugano diagrams have only qualitative significance, but much help in interpreting specta and in finding approximate value of $D_q$. For high spin complexes, the Tanabe-Sugano diagrams are similar to Orgel diagram except states of lower spin multiplicity for $d^4$, $d^5$, $d^6$ & $d^7$ which have low spin and high spin forms. For $d^1$, $d^2$, $d^3$, $d^8$ & $d^9$, the ground state is same in both weak and strong ligand fields. With increasing ligand field, state with lower multiplicity derived from a higher free ion state become ground state,

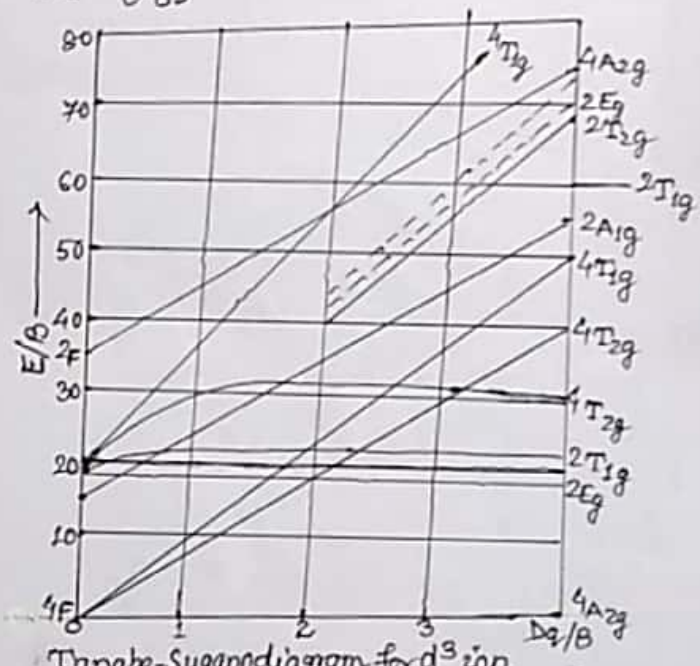
e.g; in the weak octahedral field, $d^4$ metal ions have electronic configuration $t_{2g}^3 e_g^1$ gives ground state $^5E_g$ derived from free ion term $^5D$. In strong octahedral field, the ground state configuration is $t_{2g}^4 e_g^0$ results in a triplet state $^3T_{1g}$ derived from free ion $^3H$ state. In these, higher state becomes ground state in the strong ligand field. The diagrams have a vertical line at a particular crystal field strength. Since the ground state is represented as the horizontal abscissa these diagrams are inclined after cross over region (i.e; critical $10Dq$) to make the new low spin state the horizontal abscissa.

In the Tanabe-Sugano diagram for $d^7$ system, at low field ($Dq/B'$), the $^4T_1$ ground state and other quartets are represented. Because $F^-$ (fluoride) ion is low in the spectrochemical series, the complex $[CoF_6]^{4-}$ should have a rather small value of $Dq$ and $Dq/B'$. The $B' = 0.85kK$ ($B = 0.97kK$).

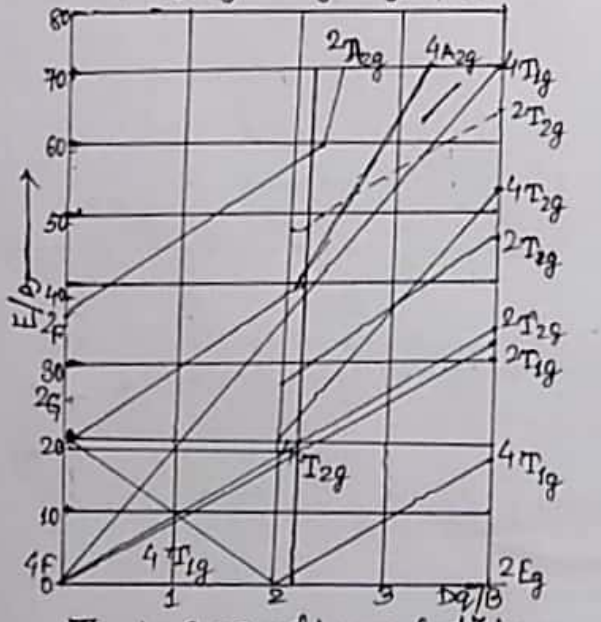
The field strength obtained was, $Dq/B' = \frac{0.8}{0.85} = 0.94$.



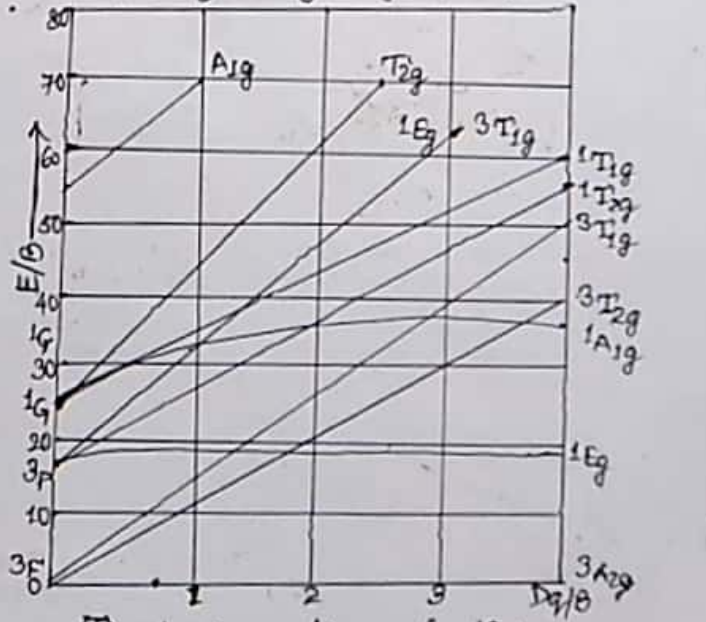

Tanabe-Sugano diagram for $d^2$ ion




Tanabe-Sugano diagram for $d^3$ ion




Tanabe-Sugano diagram for $d^7$ ion




Tanabe-Sugano diagram for $d^8$ ion.

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