Calculation of Dq, Δ_0 , B & ß by Tanabe Sugano Diagram

M. Sc. (CC-6/PAT/CSIR NET) Inorganic Chemistry

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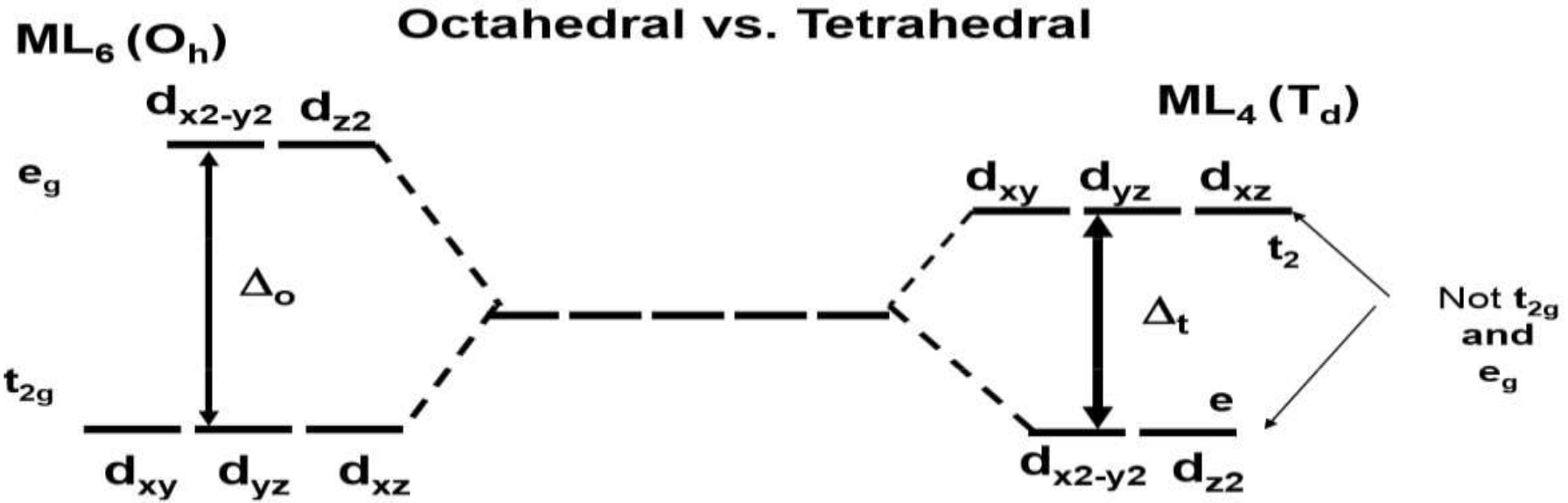
Calculation of CFSE (Δ_0), Racah Parameter (B) & Nephelauxetic Ratio (ß)

From Tanabe Sugano diagram

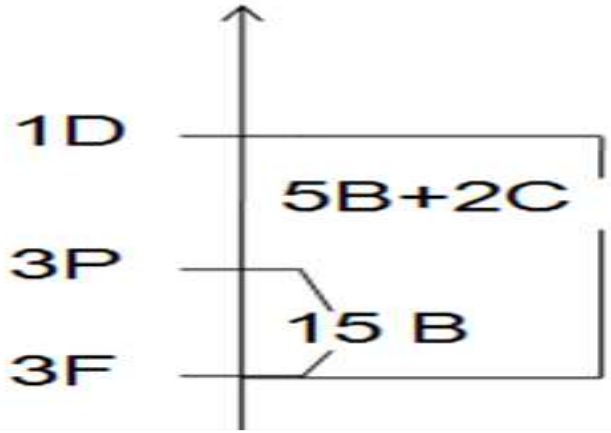
All Δ_0, Dq, B & ß are important for complex compounds & these are important to determine stability, spectral properties ionic & covalent nature of complex compound in weak field ligand & strong field ligand.

Here, Δ_0 is the energy gap between two splitted d orbital.

And Δ_0 = 10 Dq where Dq = unit for measurement of CFSE.



B is the energy gap between two terms of same multiplicity of a configuration



Nephelauxetic ratio denoted by ß = B/B' where B= racah parameter in free metal ion, B'= racah parameter in complex compound.

- It means B complex is less than B orm.
- i.e. e-e repulsfree ion.
- It means energy gap between two terms in free ion is greater than that of its complex fion between two electrons in free ion is greater than its complex.

Before calculation of CFSE (Δ_0), Racah Parameter (B) & Nephelauxetic Ratio (ß)

We must know

- $\Delta_0 = 10Dq$

therefore $1\ Dq = \Delta_0/10$ -----1

- $15B = \upsilon_3 + \upsilon_2 - 3\upsilon_1$ ----------II

$= E_3 + E_2 - 3E_1$

for d^2, d^3, d^7, d^8 system

$15B = \upsilon_1 = E_1$

for d^1, d^4, d^9, d^6 have only one peak

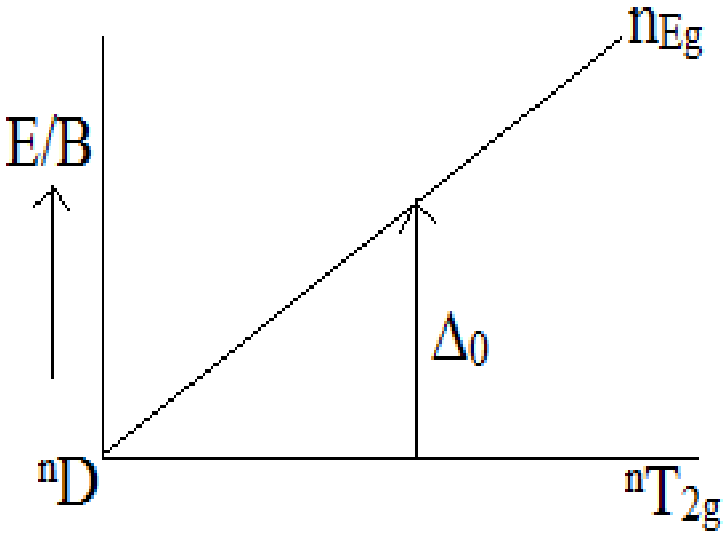
Therefore $E = \Delta_0$ or $\Delta_t = \upsilon_1\ cm^- = E_1$

Therefore $B = \upsilon_1/15$ -----III

- ß=B'/B ------IV

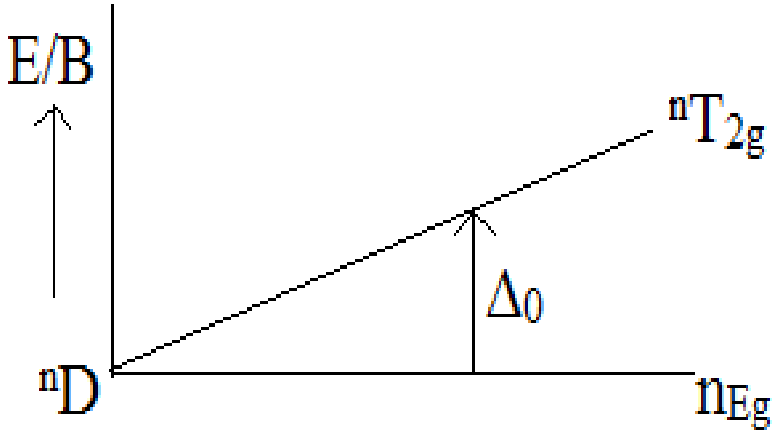
Now, let us consider TS diagram of d^n system step wise

For d^1, d^6, d^4 & d^9 we have only one transition & it gives idea about Δ_0 which is the energy gap



Δ_0/B

d^1 & d^6

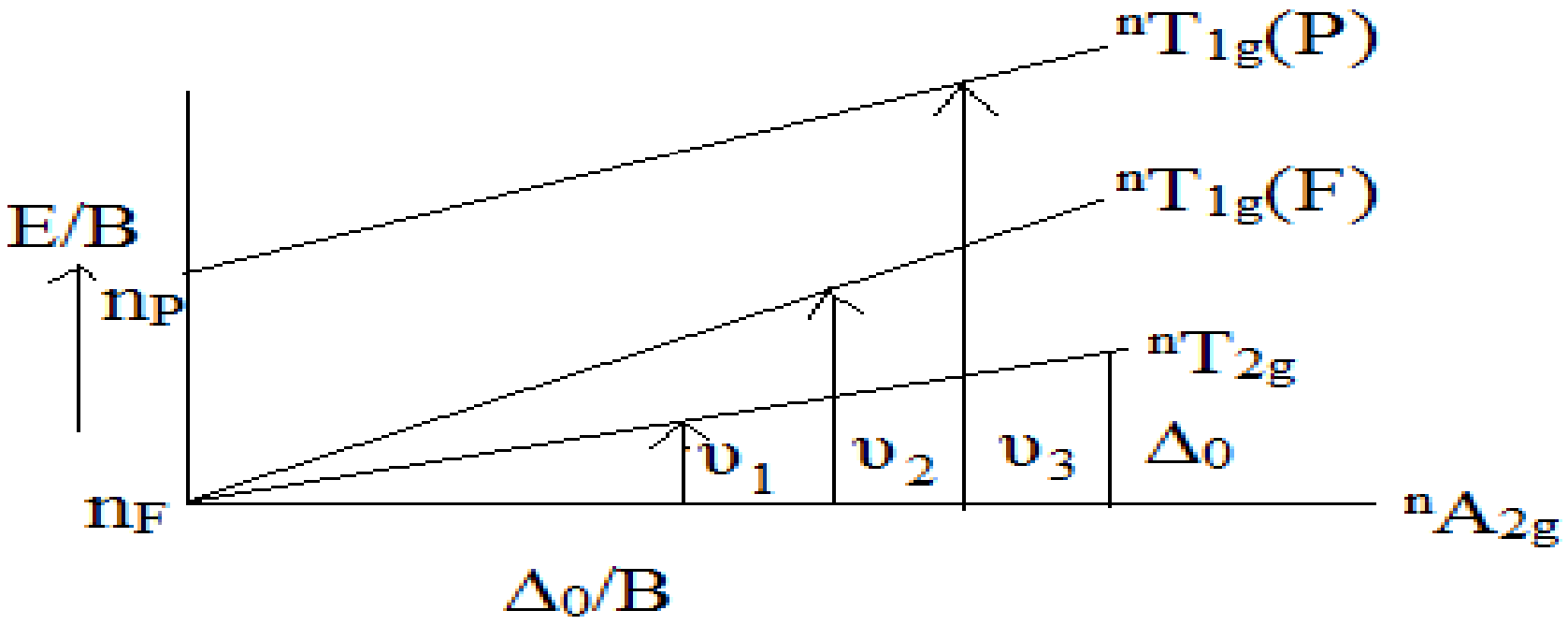


Δ_0/B

d^4 & d^9

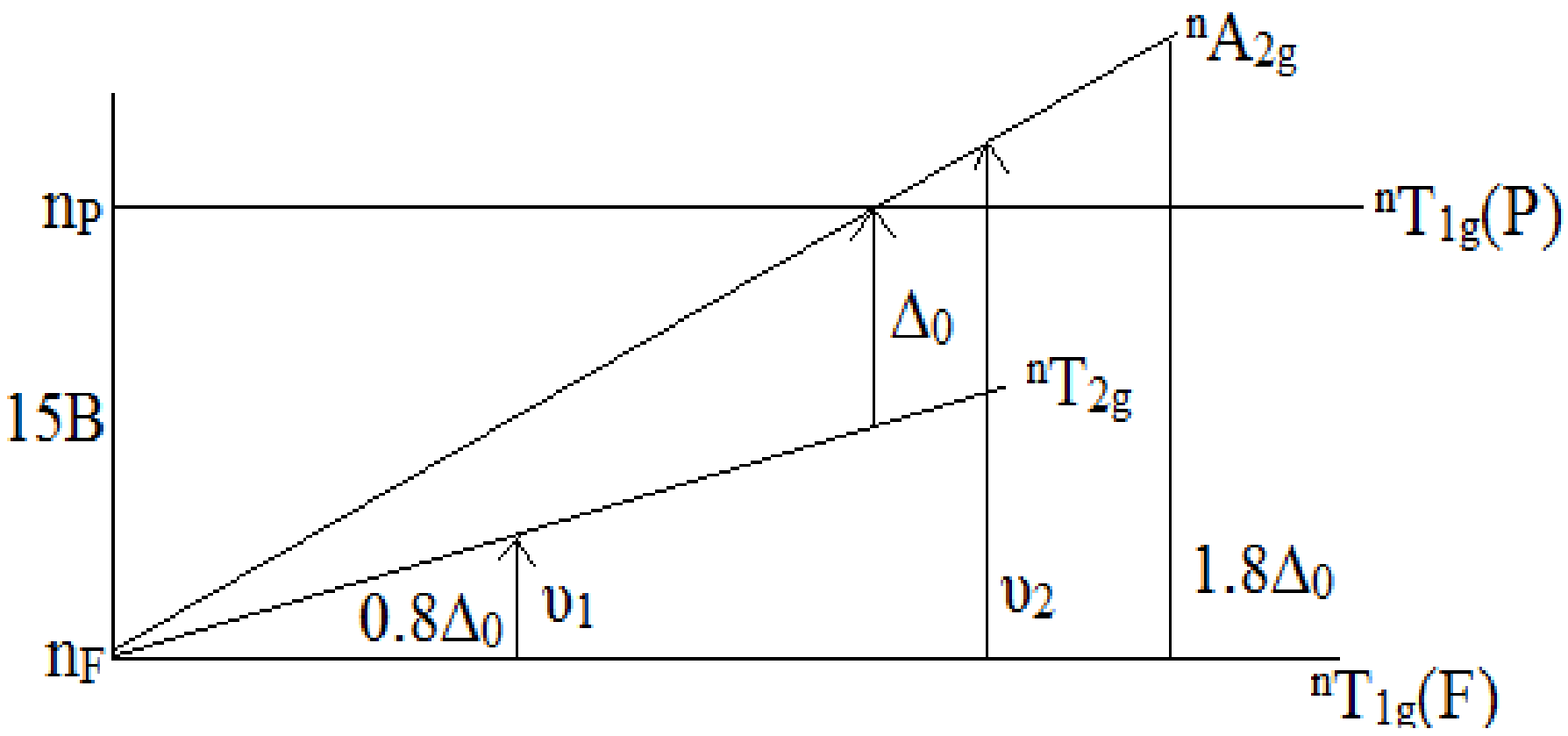
only one peak V.E therefore $\Delta_0 = \upsilon_1 = E_1$

For d^2, d^3, d^7 & d^8 H/S oh complex have 3 peaks & d^3 & d^8 have $\Delta_0 = \upsilon_1$=Energy gap of lowest transition



d^3 & d^8

For d^2 & d^7, Δ_0 = difference of energy b/w first & third transition adjacent A_{2g} & T_{2g}



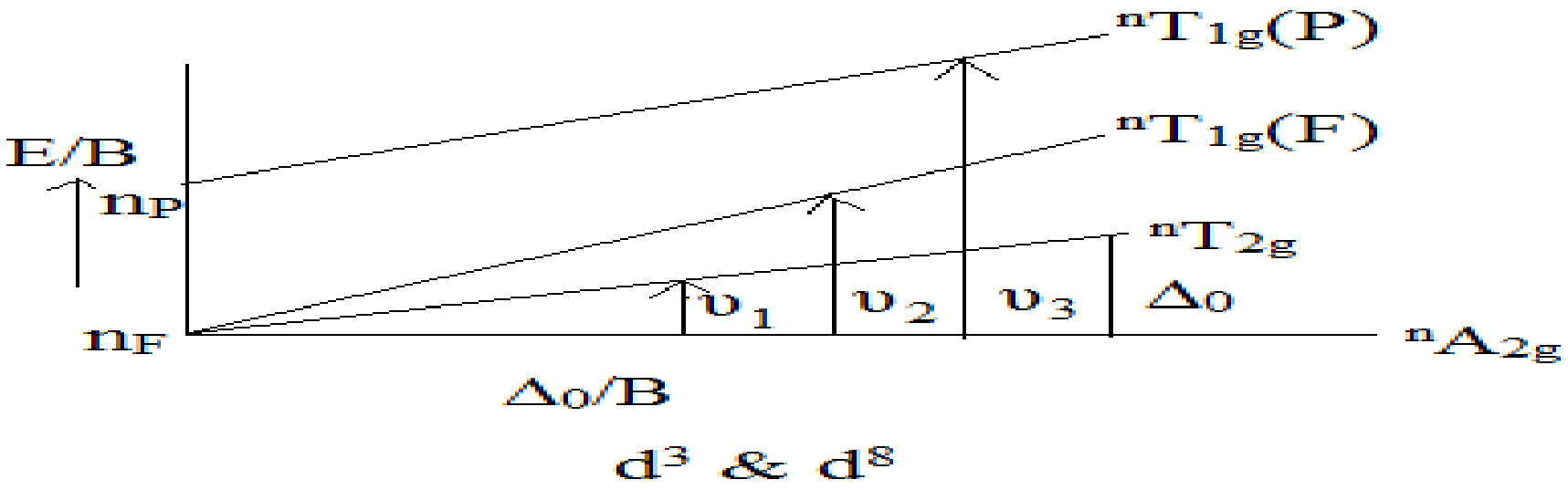
$T_{1g}F$ & $T_{1g}P$ have same symmetry so there is repulsion occurs b/w them & hence do not help to calculate accurate Δ_0 value. So we take energy gap b/w T_{2g} & A_{2g}.

Sample Problem - 1

$[Ni(H_2O)_6]^{+2}$ which gives absorption peaks at 8500, 15400 & 26000 cm^- & $B^- = 950\ cm^-$ we have to calculate value of Δ_0, B, ß

Here

Ni^{+2}- $3d^8$ have ground state term ^3F & ^3P which TS diagram is



Since lowest energy transition (υ_1)= Δ_0 = 8500 cm^-

Since 10Dq= Δ_0=8500 cm^-

therefore Dq=8500/10=850 cm

$15B=E_3+E_2-3E_1=26000+15400-3x8500=15900\ cm^-$

Therefore B=1060 cm^-

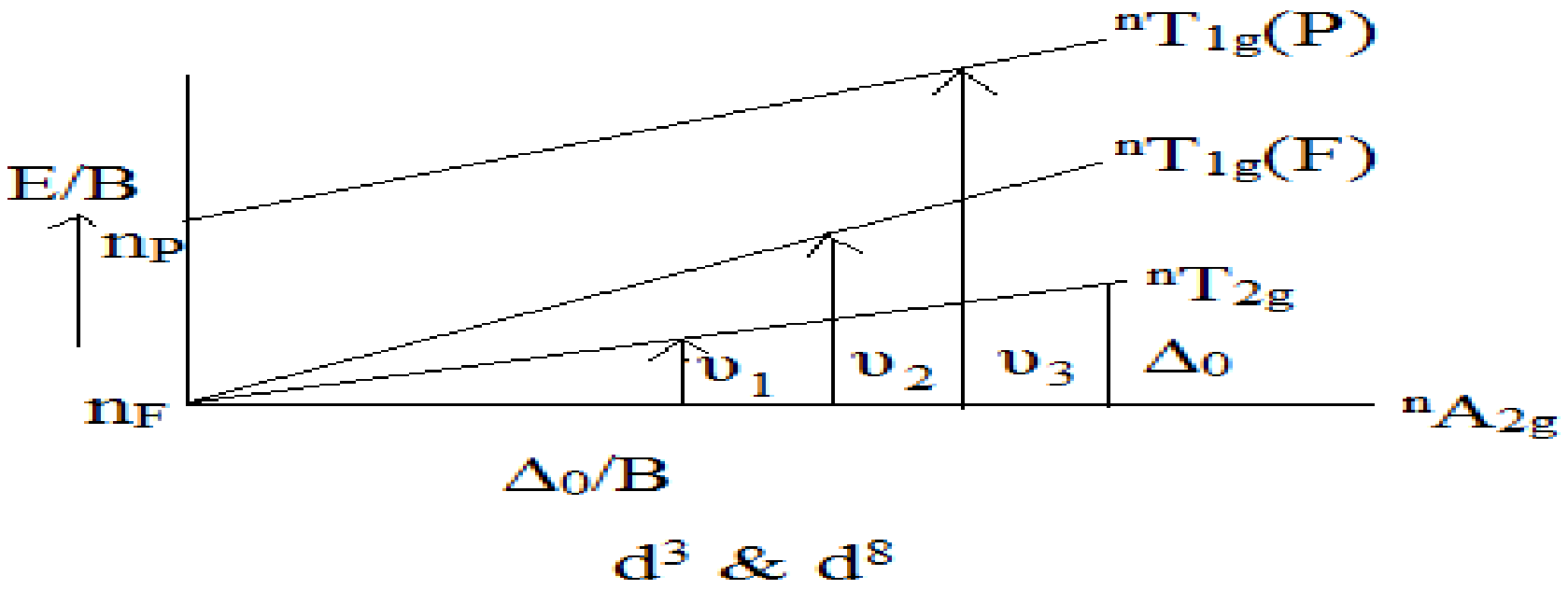
ß=B-/B=950/1060=0.93 (it is valid which less than 1)

Sample Problem -2

$[CrF_6]^{3-}$ complex gives absorption peaks 14900 cm^-, 22400 cm^- & 34800 cm^- if B value in free ion is 918 cm^-

Calculate Δ_0, B' & ß

Here, complex has Cr^{+3} ---$3d^3$ which gives 3 transition peaks



B'= 34400+22700-3x14900=12400/15=827 cm^-

$\Delta_0 = \upsilon_1$ = 14900 (lowest value of trans value of Δ_0)

ß = B'/B = 827/918 = 0.90 (less than 1 = nephelauxetic ratio)

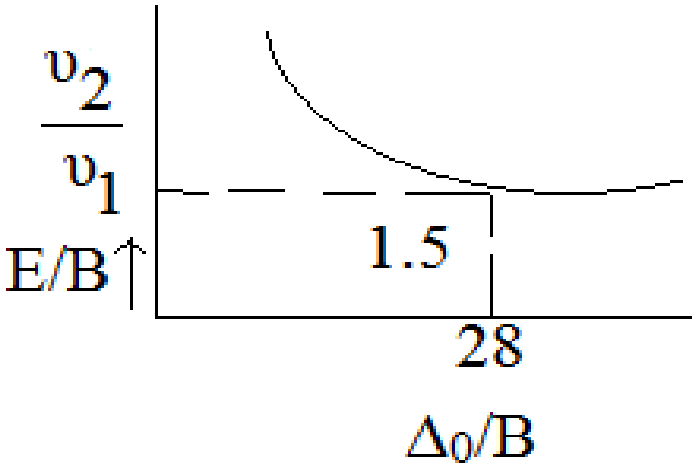
Sample Problem – 3

If a complex gives two peaks at 17200 cm^- & 25600 cm^- calculate Δ_0, Δ_t, B value if B' value is 650 cm^-

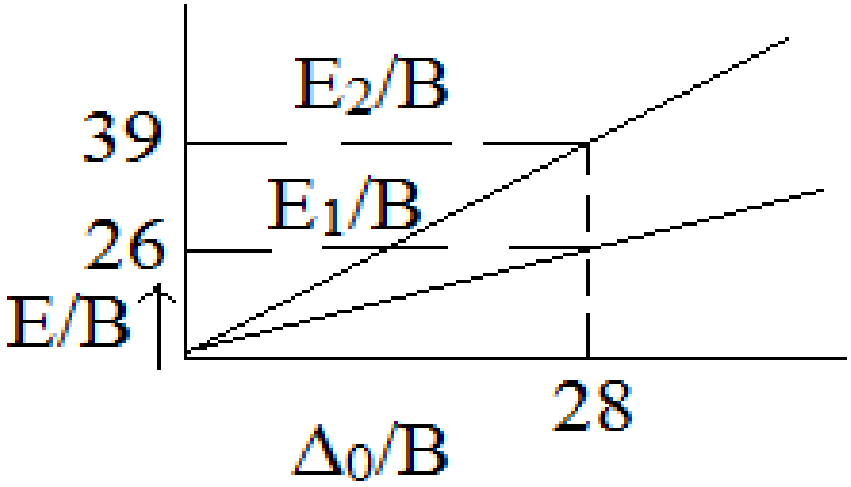
Since $\upsilon_2/\upsilon_1 = E_2/E_1 = 25600/17200 = 1.5$

Now a graph b/w E/B (υ_2/υ_1) & Δ_0/B

We get



When a graph is extra plotted b/w E/B & Δ_0/B following type of graph is obtained



E_2/B = 39 =25600/B therefore B= 660 cm^- for metal ion

E_1/B = 26

B= 17200/26=660 cm^- for metal ion

Δ_0/B=28 from first graph

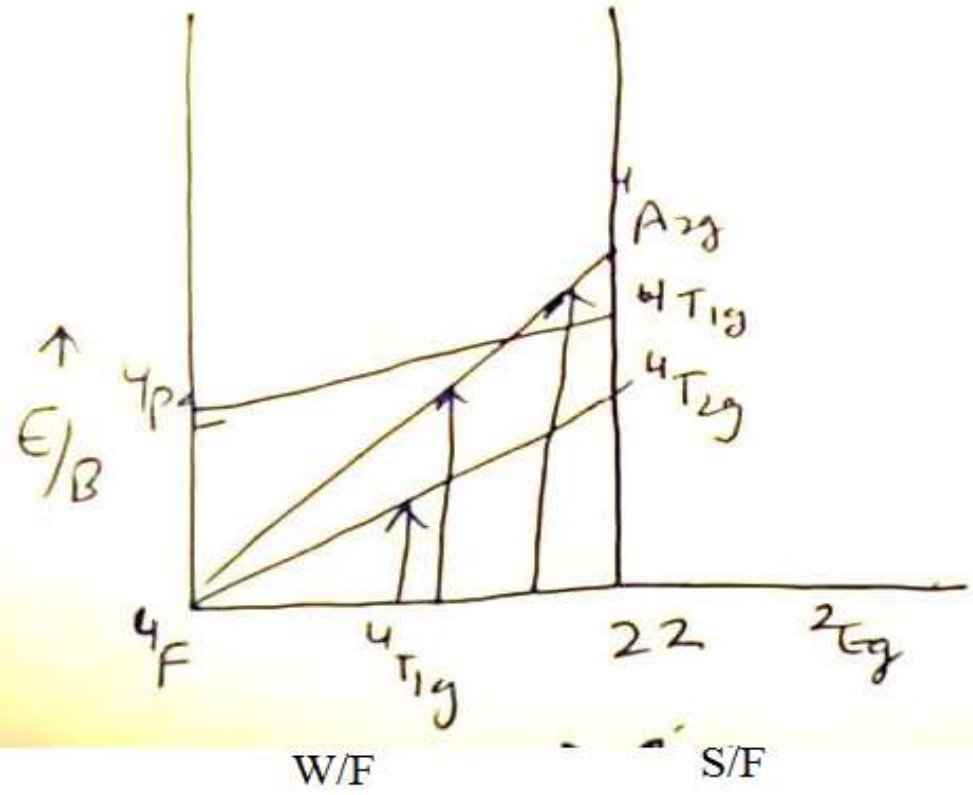
therefore Δ_0 = 28x660 = 18480 cm^-

if B' value is known than

ß=B' B = 650/660=0.98

Sample Problem – 4

A complex $[Co(NH3)_6]^{2+}$ have Δ_0= 10100 cm^-, B=920 cm^-
Calculate no. of expected absorption peaks to this complex
From question this complex has Δ_0/B=10100/920=11
In this complex Co^{+2}—$3d^7$ gives following type of TS diagram in both weak & strong field



Since this graph shows Δ_0/B value 22 at the centre of W/F & S/F & we have Δ_0/B value is 11 so surely it will be left of 22 & it gives 3 peaks. Hence we expect 3 absorption peaks in this complex.

Thank You