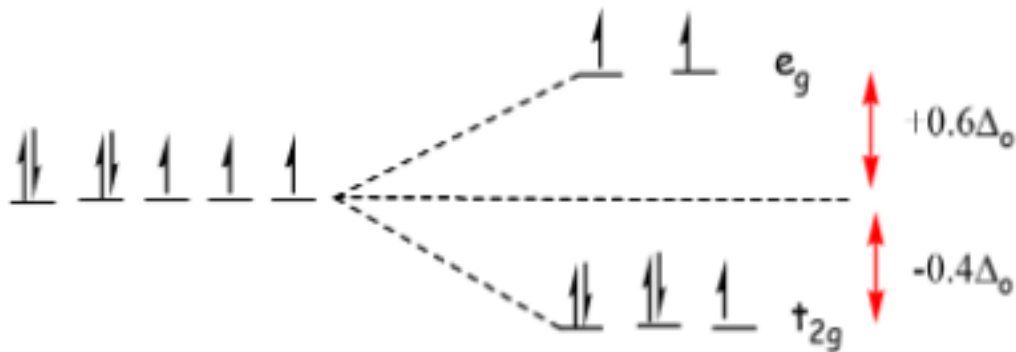


PAIRING ENERGY

- The pairing energy (P) is the energy which is required to pair two electrons in the same orbital against $e^{-1} - e^{-1}$ coulombic repulsion.
- For 3d elements, a typical value of P is about 15,000 cm^{-1} .
- 3d complexes are high spin with weak field ligands and low spin with strong field ligands.
- High valent 3d complexes (e.g., Co^{3+} complexes) tend to be low spin (large Δ_o)
- 4d and 5d complexes are always low spin (large Δ_o).

- Note that high and low spin states occur only for 3d metal complexes with between 4 and 7 d-electrons. Complexes with 1 to 3 d-electrons can accommodate all electrons in individual orbitals in the t_{2g} set. Complexes with 8, 9, or 10 d-electrons will always have completely filled t_{2g} orbitals and 2-4 electrons in the e_g set.
- The important result here is that a complex will be low spin if $\Delta_o > P$, and high spin if $\Delta_o < P$ because Δ_o depends on both the metals and the ligands, it determines the spin state of the complex.

What is the Crystal Field Stabilization Energy for a high spin d7 octahedral complex?

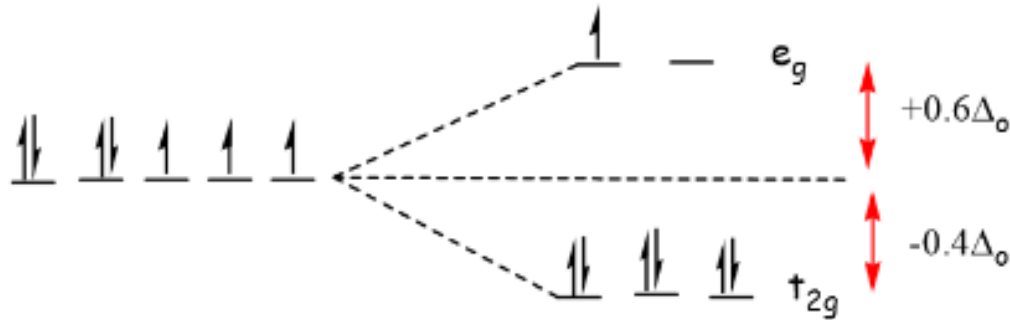


$$E_{\text{isotropic field}} = 7 \times 0 + 2P = 2P$$

$$E_{\text{ligand field}} = (5 \times -2/5\Delta_o) + (2 \times 3/5\Delta_o) + 2P = -4/5\Delta_o + 2P$$

$$\begin{aligned} CFSE &= E_{\text{ligand field}} - E_{\text{isotropic field}} \\ &= (-4/5\Delta_o + 2P) - 2P \\ &= -4/5\Delta_o \end{aligned}$$

What is the Crystal Field Stabilization Energy for a low spin d7 octahedral complex?



$$E_{\text{isotropic field}} = 7 \times 0 + 2P = 2P$$

$$\begin{aligned} E_{\text{ligand field}} &= (6 \times -2/5\Delta_o) + (1 \times 3/5\Delta_o) + 3P \\ &= -9/5\Delta_o + 3P \end{aligned}$$

$$\begin{aligned} CFSE &= E_{\text{ligand field}} - E_{\text{isotropic field}} \\ &= (-9/5\Delta_o + 3P) - 2P \\ &= -9/5\Delta_o + P \end{aligned}$$

Table 1: Crystal Field Stabilization Energies (CFSE) for high and low spin octahedral complexes

Total d-electrons	Isotropic Field	Octahedral Complex				Crystal Field Stabilization Energy	
		High Spin		Low Spin		High Spin	Low Spin
	$E_{\text{isotropic field}}$	Configuration	$E_{\text{ligand field}}$	Configuration	$E_{\text{ligand field}}$	High Spin	Low Spin
d^0	0	$t_{2g}^0 e_g^0$	0	$t_{2g}^0 e_g^0$	0	0	0
d^1	0	$t_{2g}^1 e_g^0$	$-2/5 \Delta_o$	$t_{2g}^1 e_g^0$	$-2/5 \Delta_o$	$-2/5 \Delta_o$	$-2/5 \Delta_o$
d^2	0	$t_{2g}^2 e_g^0$	$-4/5 \Delta_o$	$t_{2g}^2 e_g^0$	$-4/5 \Delta_o$	$-4/5 \Delta_o$	$-4/5 \Delta_o$
d^3	0	$t_{2g}^3 e_g^0$	$-6/5 \Delta_o$	$t_{2g}^3 e_g^0$	$-6/5 \Delta_o$	$-6/5 \Delta_o$	$-6/5 \Delta_o$
d^4	0	$t_{2g}^3 e_g^1$	$-3/5 \Delta_o$	$t_{2g}^4 e_g^0$	$-8/5 \Delta_o + P$	$-3/5 \Delta_o$	$-8/5 \Delta_o + P$
d^5	0	$t_{2g}^3 e_g^2$	$0 \Delta_o$	$t_{2g}^5 e_g^0$	$-10/5 \Delta_o + 2P$	$0 \Delta_o$	$-10/5 \Delta_o + 2P$
d^6	P	$t_{2g}^4 e_g^2$	$-2/5 \Delta_o + P$	$t_{2g}^6 e_g^0$	$-12/5 \Delta_o + 3P$	$-2/5 \Delta_o$	$-12/5 \Delta_o + P$
d^7	2P	$t_{2g}^5 e_g^2$	$-4/5 \Delta_o + 2P$	$t_{2g}^6 e_g^1$	$-9/5 \Delta_o + 3P$	$-4/5 \Delta_o$	$-9/5 \Delta_o + P$
d^8	3P	$t_{2g}^6 e_g^2$	$-6/5 \Delta_o + 3P$	$t_{2g}^6 e_g^2$	$-6/5 \Delta_o + 3P$	$-6/5 \Delta_o$	$-6/5 \Delta_o$
d^9	4P	$t_{2g}^6 e_g^3$	$-3/5 \Delta_o + 4P$	$t_{2g}^6 e_g^3$	$-3/5 \Delta_o + 4P$	$-3/5 \Delta_o$	$-3/5 \Delta_o$
d^{10}	5P	$t_{2g}^6 e_g^4$	$0 \Delta_o + 5P$	$t_{2g}^6 e_g^4$	$0 \Delta_o + 5P$	0	0

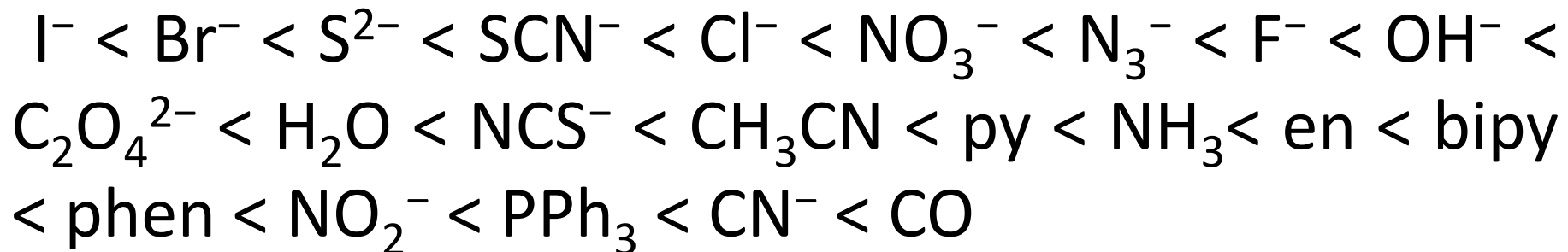
Spectrochemical Series

➤ What is Spectrochemical series and its importance?

The **spectrochemical series** is a convenient way of organizing ligands by field strength. Ligands affect the d electrons of metals, splitting degenerate energy levels into more organized levels of energy. The size of the split is called crystal field splitting parameter and abbreviated Δ .

Spectrochemical Series

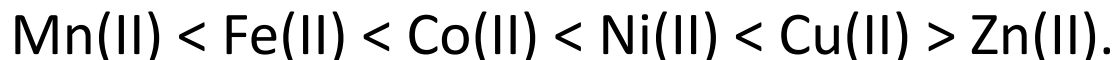
➤ Therefore the spectrochemical series is a list of ligands based on the strength of their interaction with metal ions. It is often listed, from weaker to stronger ligands, something like this:



In which py = pyridine ; en = ethylenediamine; bipy = 2,2'-bipyridine; phen = 1,10-phenanthroline; SCN means the ligand is bound via sulfur and NCS via nitrogen.

Irving-Williams Series

- The Irving-Williams Series refers to the relative stabilities of complexes formed by transition metals. According to Irving and Williams, the stability of complexes formed by divalent first-row transition metal ions generally increases across the period to a maximum stability at copper :



- The ionic radius is expected to decrease regularly from Mn(II) to Zn(II). This is the normal periodic trend and would account for the general increase in stability.
- The CFSE increases from zero for Mn(II) to a maximum at Ni(II). This makes the complexes increasingly stable. CFSE for Zn(II) is zero.
- Although the CFSE of Cu(II) is less than that of Ni(II), octahedral Cu(II) complexes are subject to the Jahn-Teller effect, which affords octahedral Cu(II) complexes additional stability.

Jahn -Teller Distortion

➤ Jahn -Teller Distortion :

For a non linear molecule in an electronically degenerate state distortion must occur to lower the symmetry, Remove the degeneracy and lower the energy.

➤ Types of Jahn -Teller Distortion :

i. Z-Out Distortion :

When two trans ligands on z-axis may be further away resulting two long bonds along z-axis and four short bonds along xy plane. This distortion is called z-out distortion.

ii. Z-In Distortion :

When two trans ligands on z-axis may be move closing resulting two short bonds along z-axis and four long bonds along xy plane. This distortion is called z-in distortion.

Examples : $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, CrF_2 , MnF_3 , $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$