

8.2.2: Crystal Field Stabilization Energy

A consequence of [Crystal Field Theory](#) is that the distribution of electrons in the d orbitals may lead to net stabilization (decrease in energy) of some complexes depending on the specific ligand field geometry and metal d-electron configurations. It is a simple matter to calculate this stabilization since all that is needed is the electron configuration and knowledge of the splitting patterns.

Definition: Crystal Field Stabilization Energy

The Crystal Field Stabilization Energy is defined as the energy of the electron configuration in the ligand field minus the energy of the electronic configuration in the isotropic field.

$$CFSE = \Delta E = E_{\text{ligand field}} - E_{\text{isotropic field}} \quad (8.2.2.1)$$

The CSFE will depend on multiple factors including:

- Geometry (which changes the d-orbital splitting patterns)
- Number of d-electrons
- [Spin Pairing Energy](#)
- Ligand character (via [Spectrochemical Series](#))

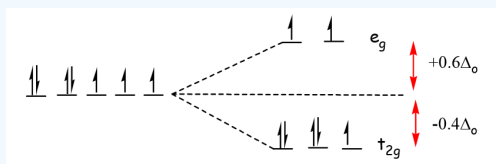
For an octahedral complex, an electron in the more stable t_{2g} subset is treated as contributing $-2/5\Delta_o$ whereas an electron in the higher energy e_g subset contributes to a destabilization of $+3/5\Delta_o$. The final answer is then expressed as a multiple of the crystal field splitting parameter Δ_o . If any electrons are paired within a single orbital, then the term P is used to represent the spin pairing energy.

✓ Example 8.2.2.1: CFSE for a high Spin d^7 complex

What is the Crystal Field Stabilization Energy for a high spin d^7 octahedral complex?

Solution

The splitting pattern and electron configuration for both isotropic and octahedral ligand fields are compared below.



The energy of the isotropic field ($E_{\text{isotropic field}}$) is

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

The energy of the octahedral ligand field $E_{\text{ligand field}}$ is

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

So via Equation 8.2.2.1, the CFSE is

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

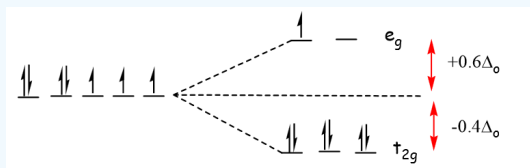
Notice that the Spin pairing Energy falls out in this case (and will when calculating the CFSE of high spin complexes) since the number of paired electrons in the ligand field is the same as that in isotropic field of the free metal ion.

✓ Example 8.2.2.2: CFSE for a Low Spin d^7 complex

What is the Crystal Field Stabilization Energy for a low spin d^7 octahedral complex?

Solution

The splitting pattern and electron configuration for both isotropic and octahedral ligand fields are compared below.



The energy of the isotropic field is the same as calculated for the high spin configuration in Example 1:

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

The energy of the octahedral ligand field $E_{\text{ligand field}}$ is

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

So via Equation 8.2.2.1, the CFSE is

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

Adding in the pairing energy since it will require extra energy to pair up one extra group of electrons. This appears more a more stable configuration than the high spin d^7 configuration in Example 8.2.2.1, but we have then to take into consideration the Pairing energy P to know definitely, which varies between $200 - 400 \text{ kJ mol}^{-1}$ depending on the metal.

Table 8.2.2.1: 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	$E_{\text{ligand field}}$		
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

P is the [spin pairing energy](#) and represents the energy required to pair up electrons within the same orbital. For a given metal ion P (pairing energy) is constant, but it does not vary with ligand and [oxidation state](#) of the metal ion).

Octahedral Preference

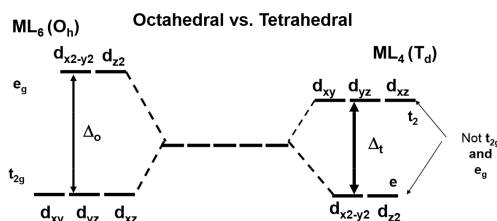
Similar CFSE values can be constructed for non-octahedral ligand field geometries once the knowledge of the d-orbital splitting is known and the electron configuration within those orbitals known, e.g., the tetrahedral complexes in Table 8.2.2.2 These energies geometries can then be contrasted to the octahedral CFSE to calculate a thermodynamic preference (Enthalpy-wise) for a metal-ligand combination to favor the octahedral geometry. This is quantified via a Octahedral Site Preference Energy defined below.

Definition: Octahedral Site Preference Energies

The Octahedral Site Preference Energy (OSPE) is defined as the difference of CFSE energies for a non-octahedral complex and the octahedral complex. For comparing the preference of forming an octahedral ligand field vs. a tetrahedral ligand field, the OSPE is thus:

$$OSPE = CFSE_{(oct)} - CFSE_{(tet)} \quad (8.2.2.2)$$

The OSPE quantifies the preference of a complex to exhibit an octahedral geometry vs. a tetrahedral geometry.



Note: the conversion between Δ_o and Δ_t used for these calculations is:

$$\Delta_t \approx \frac{4}{9} \Delta_o \quad (8.2.2.3)$$

which is applicable for comparing octahedral and tetrahedral complexes that involve same ligands only.

Table 8.2.2.2: Octahedral Site Preference Energies (OSPE)

Total d-electrons	CFSE(Octahedral)		CFSE(Tetrahedral)		OSPE (for high spin complexes)**
	High Spin	Low Spin	Configuration	Always High Spin*	
d ⁰	0 Δ_o	0 Δ_o	e ⁰	0 Δ_t	0 Δ_o
d ¹	-2/5 Δ_o	-2/5 Δ_o	e ¹	-3/5 Δ_t	-6/45 Δ_o
d ²	-4/5 Δ_o	-4/5 Δ_o	e ²	-6/5 Δ_t	-12/45 Δ_o
d ³	-6/5 Δ_o	-6/5 Δ_o	e ² t ₂ ¹	-4/5 Δ_t	-38/45 Δ_o
d ⁴	-3/5 Δ_o	-8/5 Δ_o + P	e ² t ₂ ²	-2/5 Δ_t	-19/45 Δ_o
d ⁵	0 Δ_o	-10/5 Δ_o + 2P	e ² t ₂ ³	0 Δ_t	0 Δ_o
d ⁶	-2/5 Δ_o	-12/5 Δ_o + P	e ³ t ₂ ³	-3/5 Δ_t	-6/45 Δ_o
d ⁷	-4/5 Δ_o	-9/5 Δ_o + P	e ⁴ t ₂ ³	-6/5 Δ_t	-12/45 Δ_o
d ⁸	-6/5 Δ_o	-6/5 Δ_o	e ⁴ t ₂ ⁴	-4/5 Δ_t	-38/45 Δ_o
d ⁹	-3/5 Δ_o	-3/5 Δ_o	e ⁴ t ₂ ⁵	-2/5 Δ_t	-19/45 Δ_o
d ¹⁰	0	0	e ⁴ t ₂ ⁶	0 Δ_t	0 Δ_o

P is the [spin pairing energy](#) and represents the energy required to pair up electrons within the same orbital.

Tetrahedral complexes are always high spin since the splitting is appreciably smaller than P (Equation [8.2.2.3](#)).

After conversion with Equation 8.2.2.3 The data in Tables 8.2.2.1 and 8.2.2.2 are represented graphically by the curves in Figure 8.2.2.1 below for the high spin complexes only. The low spin complexes require knowledge of P to graph.

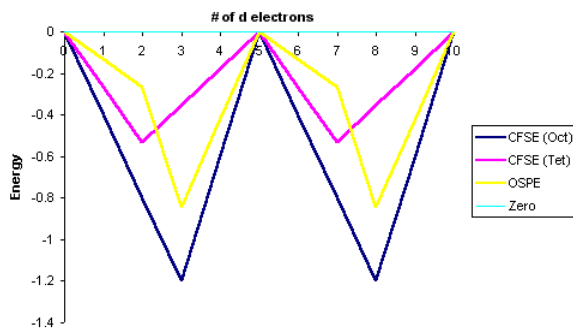


Figure 8.2.2.1: Crystal Field Stabilization Energies for both octahedral fields ($CFSE_{oct}$) and tetrahedral fields ($CFSE_{tet}$). Octahedral Site Preference Energies (OSPE) are in yellow. This is for high spin complexes.

From a simple inspection of Figure 8.2.2.1 the following observations can be made:

- The OSPE is *small* in d^1 , d^2 , d^5 , d^6 , d^7 complexes and other factors influence the stability of the complexes including steric factors
- The OSPE is *large* in d^3 and d^8 complexes which strongly favor octahedral geometries

Applications

The "double-humped" curve in Figure 8.2.2.1 is found for various properties of the first-row transition metals, including Hydration and [Lattice energies](#) of the M(II) ions, ionic radii as well as the stability of M(II) complexes. This suggests that these properties are somehow related to Crystal Field effects.

In the case of Hydration Energies describing the [complexation](#) of water ligands to a bare metal ion:

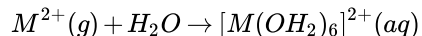


Table 8.2.2.3 and Figure 8.2.2.1 shows this type of curve. Note that in any series of this type not all the data are available since a number of ions are not very stable in the M(II) state.

Table 8.2.2.3: Hydration energies of M^{2+} ions

M	$\Delta H^\circ/\text{kJmol}^{-1}$	M	$\Delta H^\circ/\text{kJmol}^{-1}$
Ca	-2469	Fe	-2840
Sc	no stable 2+ ion	Co	-2910
Ti	-2729	Ni	-2993
>V	-2777	Cu	-2996
Cr	-2792	Zn	-2928
Mn	-2733		

Graphically the data in Table 2 can be represented by:

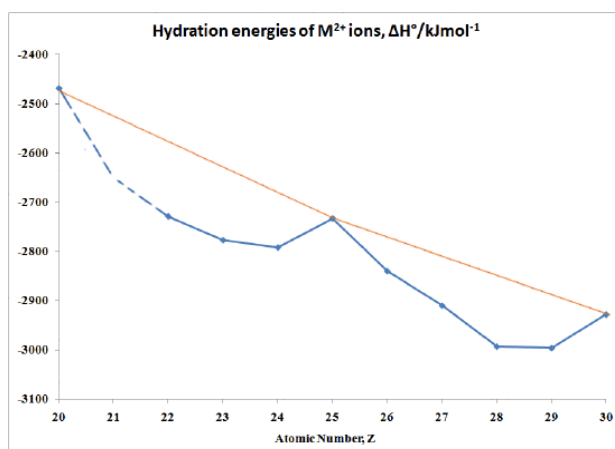


Figure 8.2.2.2: hydration energies of M^{2+} ions

Contributors and Attributions

- [Prof. Robert J. Lancashire](#) (The Department of Chemistry, University of the West Indies)

8.2.2: Crystal Field Stabilization Energy is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [Crystal Field Stabilization Energy](#) is licensed [CC BY-NC-SA 4.0](#).