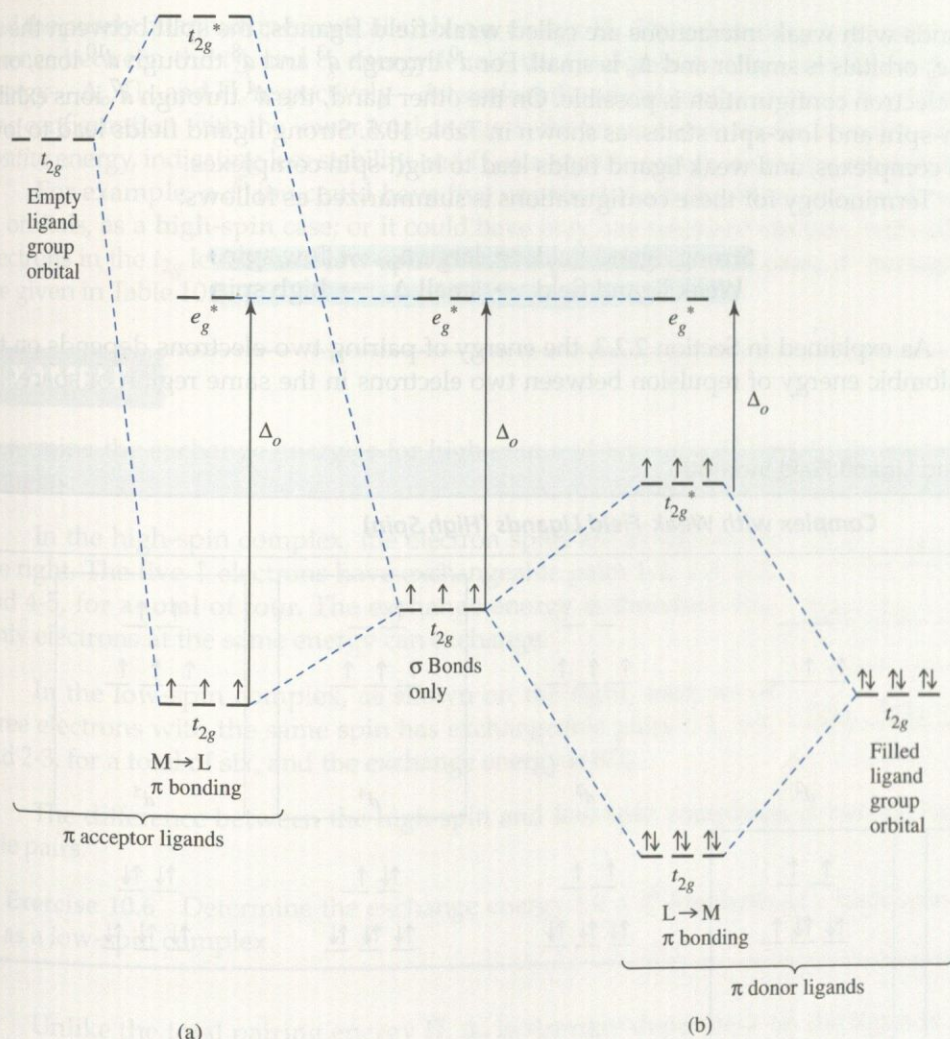**FIGURE 10.11** Effects of $\pi$ Bonding on $\Delta_o$ using a $d^3$ Ion.



Overall, filled $\pi^*$ or $p$ orbitals on ligands, frequently with relatively low energy, result in L $\longrightarrow$ M $\pi$ bonding and a smaller $\Delta_o$ for the complex. Empty higher-energy $\pi$ or $d$ orbitals on the ligands result in M $\longrightarrow$ L $\pi$ bonding and a larger $\Delta_o$ for the complex. Ligand-to-metal $\pi$ bonding usually gives decreased stability for the complex, favoring high-spin configurations; metal-to-ligand $\pi$ bonding usually gives increased stability and favors low-spin configurations.

Part of the stabilizing effect of $\pi$ back-bonding is a result of transfer of negative charge away from the metal ion. The positive ion accepts electrons from the ligands to form $\sigma$ bonds. The metal is then left with a surplus of negative charge. When the $\pi$ orbitals can be used to transfer part of this charge back to the ligands, the overall stability is improved. The $\pi$-acceptor ligands that can participate in $\pi$ back-bonding are extremely important in organometallic chemistry and will be discussed further in Chapter 13.

## 10.3.2 Orbital Splitting and Electron Spin

In octahedral coordination complexes, electrons from the ligands fill all six bonding molecular orbitals, and any electrons from the metal ion occupy the $t_{2g}$ and $e_g^*$ orbitals. Ligands whose orbitals interact strongly with the metal orbitals are called **strong-field ligands**; with these, the split between the $t_{2g}$ and $e_g^*$ orbitals is large, so $\Delta_o$ is large.

Ligands with weak interactions are called **weak-field ligands**; the split between the $t_{2g}$ and $e_g$ orbitals is smaller and $\Delta_o$ is small. For $d^0$ through $d^3$ and $d^8$ through $d^{10}$ ions, only one electron configuration is possible. On the other hand, the $d^4$ through $d^7$ ions exhibit **high-spin** and **low-spin** states, as shown in Table 10.5. Strong ligand fields lead to low-spin complexes, and weak ligand fields lead to high-spin complexes.

Terminology for these configurations is summarized as follows:

$$\text{Strong ligand field} \;\rightarrow\; \text{large } \Delta_o \;\rightarrow\; \text{low spin}$$
$$\text{Weak ligand field} \;\rightarrow\; \text{small } \Delta_o \;\rightarrow\; \text{high spin}$$

As explained in Section 2.2.3, the energy of pairing two electrons depends on the Coulombic energy of repulsion between two electrons in the same region of space, $\Pi_c$,

**TABLE 10.5  Spin States and Ligand Field Strength**

*Complex with Weak-Field Ligands (High Spin)*



*Complex with Strong Field Ligands (Low Spin)*

and the purely quantum mechanical exchange energy, $\Pi_e$. The relationship between the difference between the $t_{2g}$ and $e_g$ energy levels, the Coulombic energy, and the exchange energy—$\Delta_o$, $\Pi_c$, and $\Pi_e$ respectively—determines the orbital configuration of the electrons. The configuration with the lower total energy is the ground state for the complex. $\Pi_c$ is a *positive* energy, indicating less stability, and $\Pi_e$ is a *negative* energy, indicating more stability.

For example, a $d^5$ ion could have five unpaired electrons, three in $t_{2g}$ and two in $e_g$ orbitals, as a **high-spin** case; or it could have only one unpaired electron, with all five electrons in the $t_{2g}$ levels, as a **low-spin** case. The possibilities for all cases, $d^1$ through $d^{10}$, are given in Table 10.5.
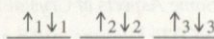
## EXAMPLE

Determine the exchange energies for high-spin and low-spin $d^6$ ions in an octahedral complex.

In the high-spin complex, the electron spins are as shown on the right. The five ↑ electrons have exchangeable pairs 1-2, 1-3, 2-3, and 4-5, for a total of four. The exchange energy is therefore $4\Pi_e$. Only electrons at the same energy can exchange.

$$\underline{\uparrow_4} \quad \underline{\uparrow_5}$$

$$\underline{\uparrow_1\downarrow_1} \quad \underline{\uparrow_2} \quad \underline{\uparrow_3}$$
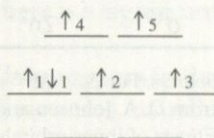
In the low-spin complex, as shown on the right, each set of three electrons with the same spin has exchangeable pairs 1-2, 1-3, and 2-3, for a total of six, and the exchange energy is $6\Pi_e$.

$$\underline{\phantom{xx}} \quad \underline{\phantom{xx}}$$

$$\underline{\uparrow_1\downarrow_1} \quad \underline{\uparrow_2\downarrow_2} \quad \underline{\uparrow_3\downarrow_3}$$

The difference between the high-spin and low-spin complexes is two exchangeable pairs.

▶ **Exercise 10.6**   Determine the exchange energy for a $d^5$ ion, both as a high-spin and as a low-spin complex.

Unlike the total pairing energy $\Pi$, $\Delta_o$ is strongly dependent on the ligands and on the metal. Table 10.6 presents values of $\Delta_o$ for aqueous ions, in which water is a relatively weak-field ligand (small $\Delta_o$). The number of unpaired electrons in the complex depends on the balance between $\Delta_o$ and $\Pi$:

When $\Delta_o > \Pi$, there is a net loss in energy (an increase in stability) on pairing electrons in the lower levels; the low-spin configuration is more stable;

When $\Delta_o < \Pi$, the total energy is lower with more unpaired electrons; the high-spin configuration is more stable.

In Table 10.6, only $Co^{3+}$ has $\Delta_o$ near the size of $\Pi$, and $[Co(H_2O)_6]^{3+}$ is the only low-spin aqua complex. All the other first-row transition metal ions require a stronger field ligand than water for a low-spin configuration. The tabulated $\Delta_o$ and $\Pi$ energies for $[Co(H_2O)_6]^{3+}$ indicate that the relative magnitudes of these values provide a useful conceptual framework to rationalize high and low spin states but that experimental measurements, such as the determination of magnetic susceptibility, provide the most reliable data for assessing electronic configurations.

In general, the strength of the ligand–metal interaction is greater for metals having higher charges. This can be seen in the table: $\Delta_o$ for 3+ ions is larger than for 2+ ions. Also, values for $d^5$ ions are smaller than for $d^4$ and $d^6$ ions.

Another factor that influences electron configurations is the position of the metal in the periodic table. Metals from the second and third transition series form low-spin complexes more readily than metals from the first transition series. This is a consequence of

**TABLE 10.6  Orbital Splitting ($\Delta_o$) and Mean Pairing Energy ($\Pi$) for Aqueous Ions[a]**

| | Ion | $\Delta_o$ | $\Pi$ | Ion | $\Delta_o$ | $\Pi$ |
|---|---|---|---|---|---|---|
| $d^1$ | | | | $Ti^{3+}$ | 18,800 | |
| $d^2$ | | | | $V^{3+}$ | 18,400 | |
| $d^3$ | $V^{2+}$ | 12,300 | | $Cr^{3+}$ | 17,400 | |
| $d^4$ | $Cr^{2+}$ | 9,250 | 23,500 | $Mn^{3+}$ | 15,800 | 28,000 |
| $d^5$ | $Mn^{2+}$ | 7,850[b] | 25,500 | $Fe^{3+}$ | 14,000 | 30,000 |
| $d^6$ | $Fe^{2+}$ | 9,350 | 17,600 | $Co^{3+}$ | 16,750 | 21,000 |
| $d^7$ | $Co^{2+}$ | 8,400 | 22,500 | $Ni^{3+}$ | | 27,000 |
| $d^8$ | $Ni^{2+}$ | 8,600 | | | | |
| $d^9$ | $Cu^{2+}$ | 7,850 | | | | |
| $d^{10}$ | $Zn^{2+}$ | 0 | | | | |

*Sources:* For $\Delta_o$:  $M^{2+}$ data from D. A. Johnson and P. G. Nelson, *Inorg. Chem.*, **1995**, *34*, 5666; $M^{3+}$ data from D. A. Johnson and P. G. Nelson, *Inorg. Chem.*, **1999**, *38*, 4949. For $\Pi$: Data from D. S. McClure, The Effects of Inner-orbitals on Thermodynamic Properties, in T. M. Dunn, D. S. McClure, and R. G. Pearson, *Some Aspects of Crystal Field Theory*, Harper & Row, New York, 1965, p. 82.

NOTE: [a]Values given are in $cm^{-1}$.

[b] Estimated value

two cooperating effects: one is the greater overlap between the larger $4d$ and $5d$ orbitals and the ligand orbitals, and the other is a decreased pairing energy due to the larger volume available for electrons in the $4d$ and $5d$ orbitals as compared with $3d$ orbitals.

## 10.3.3 Ligand Field Stabilization Energy

The difference between (1) the total energy of a coordination complex with the electron configuration resulting from ligand field splitting of the orbitals and (2) the total energy for the same complex with all the $d$ orbitals if they were equally populated is called the **ligand field stabilization energy (LFSE)**. The LFSE represents the stabilization of the $d$ electrons because of the metal–ligand environment. A common way to calculate LFSE is shown for $d^4$ in Figure 10.12.

The interaction of the $d$ orbitals of the metal with the ligand orbitals results in lower energy for the $t_{2g}$ set of orbitals ($-\frac{2}{5}\Delta_o$ relative to the average energy of all $t_{2g}$ and $e_g$ orbitals) and increased energy for the $e_g$ set ($\frac{3}{5}\Delta_o$). The total energy of a one-electron system would then be $-\frac{2}{5}\Delta_o$, and the total energy of a high-spin four-electron system would be $\frac{3}{5}\Delta_o + 3(-\frac{2}{5}\Delta_o) = -\frac{3}{5}\Delta_o$. An alternative method of arriving at these energies is given by Cotton.[16]

▶ **Exercise 10.7**  Determine the LFSE for a $d^6$ ion for both high-spin and low-spin cases.

Table 10.7 has the LFSE values for $\sigma$-bonded octahedral complexes with 1-10 electrons in both high- and low-spin arrangements. The final columns show the pairing energies and

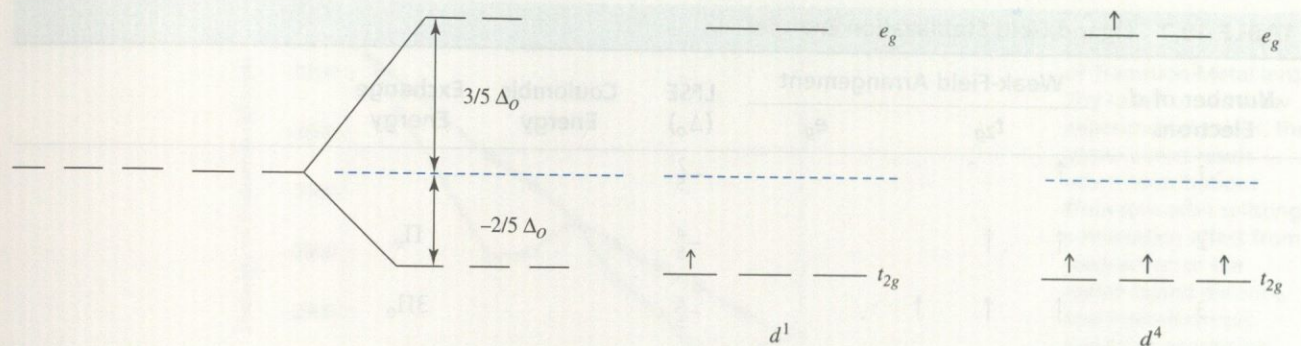[16] F. A. Cotton, *J. Chem. Educ.*, **1964**, *41*, 466.

**FIGURE 10.12** Splitting of Orbital Energies in a Ligand Field.

the difference in LFSE between low-spin and high-spin complexes with the same total number of $d$ electrons. For one to three and eight to ten electrons, there is no difference in the number of unpaired electrons or the LFSE. For four to seven electrons, there is a significant difference in both, and high- and low-spin arrangements are possible.

The most commonly cited example of LFSE in thermodynamic data appears in the exothermic enthalpy of hydration of bivalent ions of the first transition series, usually assumed to have six waters of hydration:

$$M^{2+} (g) + 6\,H_2O(l) \longrightarrow [M(H_2O)_6]^{2+} (aq)$$
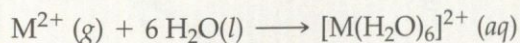
Ions with spherical symmetry should have $\Delta H$ becoming increasingly exothermic (more negative) continuously across the transition series, because of the decreasing radius of the ions with increasing nuclear charge and corresponding increase in electrostatic attraction for the ligands. Instead, the enthalpies show the characteristic double-loop shape shown in Figure 10.13. The almost linear curve of the "corrected" enthalpies is expected for ions with decreasing radius. The differences between this curve and the double-humped experimental values are approximately equal to the LFSE values in Table 10.7 for high-spin complexes,[17] with additional smaller corrections for spin-orbit splittings (0 to 16 kJ/mol), a relaxation effect caused by contraction of the metal–ligand distance (0 to 24 kJ/mol), and an interelectronic repulsion energy that depends on the exchange interactions between electrons with the same spins (0 to –19 kJ/mol for $M^{2+}$, 0 to –156 kJ/mol for $M^{3+}$).[18] The latter three effects are relatively minimal, but they improve the shape of the curve for the corrected values significantly. In the case of the hexaaqua and hexafluoro complexes of the 3+ transition-metal ions, the interelectronic repulsion energy, sometimes called the *nephelauxetic effect*, is larger and is required to remove the deviation from a smooth curve through the $d^0$, $d^5$, and $d^{10}$ values.

Why do we care about LFSE? There are two principal reasons. First, it provides a more quantitative approach to the high-spin–low-spin electron configurations, helping predict which configuration will be more likely. Second, it is the basis for our discussion of the spectra of these complexes in Chapter 11. Measurements of $\Delta_o$ are commonly provided in studies of these complexes, with a goal of eventually allowing a better and more quantitative understanding of metal-ligand interactions. At this point, the relative sizes of $\Delta_o$, $\Pi_c$, and $\Pi_e$ are the important features.

[17] L. E. Orgel, *J. Chem. Soc.*, **1952**, 4756; P. George and D. S. McClure, *Prog. Inorg. Chem.*, **1959**, 1, 381.
[18] D. A. Johnson and P. G. Nelson, *Inorg. Chem.* **1995**, *34*, 3253; **1995**, 34, 5666; **1999**, 38, 4949.

*Fourth Edition*

# INORGANIC CHEMISTRY

**Gary L. Miessler**

*St. Olaf College Northfield, Minnesota*

**Donald A. Tarr**

*St. Olaf College Northfield, Minnesota*