

aspherical occupation of the partially filled $3d$ shell. The latter cause, when present, is dominant because of the relatively short range of the quadrupolar forces. In a free ion, and normally in an ionic compound, the $3d$ orbitals are filled to give maximum multiplicity, according to Hund's rule. A high-spin ferric ion with five $3d$ electrons, one in each of five available levels, presents a spherically symmetric field, so any quadrupole splitting depends strictly on the noncubic arrangement of the ligands. Since the extra $3d$ electron of the ferrous ion is never *smeared out* in a spherically symmetric manner over the $3d$ orbitals, high spin ferrous systems exhibit large quadrupole splittings. If the interaction between ligand and metal is sufficiently strong, it may be energetically advantageous to pair the electron spins. A low-spin ferrous ion exhibits little or no quadrupole splitting, while a low-spin ferric ion exhibits significantly more.

Typical values for isomer shifts and quadrupole splittings are presented in Table I. The high-spin ferrous ion [Fe(II)] has a relatively large isomer shift, which corresponds to a relatively low electron density at the nucleus. This is consistent with the fact that there are six $3d$ electrons shielding the $3s$ electrons. As discussed above, there is a large quadrupole splitting. The ferric ion [Fe(III)] exhibits a significantly smaller isomer shift (larger electron density at the nucleus). In large part this is due to the decreased shielding of the $3s$ electrons, since there are nominally only five $3d$ electrons. The quadrupole splitting is usually modest unless the external symmetry is very far from cubic. There exist higher oxidation states of iron—Fe(IV), nominally a $3d^4$ ion, and Fe(VI), nominally a $3d^2$ ion. These exhibit increased electron density at the nucleus as is expected from the reduced shielding of the $3s$ orbitals. Their quadrupole splitting has not been analyzed in any detail.

TABLE I
TYPICAL ISOMER SHIFT AND QUADRUPOLE SPLITTING
(mm/sec)

	Isomer Shift (Rel. to Iron Metal)	Quadrupole Splitting
Fe(II) high spin	1.3–1.4	2.0–3.0
Fe(III) high spin	0.3–0.5	0.3–0.5
Fe(IV) (ferrate)	(–0.1)–(0.0)	—
Fe(VI) (ferrate)	(–0.9)–(–0.8)	—
Ferrocyanide	(–0.1)–(0.0)	~ 0
Ferricyanide	(–0.1)–(0.0)	0.3–0.6
Nitroprusside	(–0.3)–(–0.2)	1.6–2.0

By far, the most widely studied of the low-spin compounds of iron are the ferrocyanides, ferricyanides, and substituted cyanides. Although these nominally contain six $3d$ electrons (five for the ferricyanides) they exhibit a relatively small isomer shift (high electron density at the nucleus), because the $3d$ electrons are very strongly delocalized, due to covalent interaction with the ligand orbitals. This fact will be of great importance in the latter part of the paper. The quadrupole splittings can be accounted for on the basis of our earlier discussion—the large value for the nitroprusside ion is caused by the strongly distorted ligand field.

A $3d$ electron on a free ion of iron can exist in a series of fivefold degenerate energy levels. The difference in energy between the ground state and the excited states is due to the difference in interelectronic repulsion in the various configurations. Their energy differences can most conveniently be expressed in terms of the Racah parameters A , B , and C . In a field of less than spherical symmetry, the degeneracy is partially removed. For octahedral symmetry, one obtains a threefold degenerate (t_{2g}) set of levels with orbitals concentrated between the ligands (π symmetry) and a doubly degenerate set of (e_g) levels of higher energy, having σ symmetry. The splitting between these levels is a measure of the ligand field called $10 Dq$ or Δ . For other symmetries, the splittings vary but none of the phenomena discussed here would be qualitatively different. Optical transitions of relatively low-intensity measure Δ or combinations of Δ and the Racah parameters B and C in the complex. For a ferrous ion in a typical ionic crystal, Δ values are on the order of $8000\text{--}9000\text{ cm}^{-1}$ (1–1.1 eV), while $B \cong C/4$ is of the order of 900 cm^{-1} . If the ligand field reaches a value of $14,000\text{--}16,000\text{ cm}^{-1}$, one may obtain a spin paired state, as mentioned above. The ferrocyanides and related compounds exhibit a ligand field $\Delta \sim 32,000\text{--}36,000\text{ cm}^{-1}$ and a value of the Racah parameter $B \sim 400\text{ cm}^{-1}$. The low value of the interelectronic repulsion parameter indicates the strong delocalization of the $3d$ orbitals and is consistent with the low value of the isomer shift mentioned above.

There exists, in most transition metal ion complexes, a very intense transition with a peak center at $24,000\text{--}40,000\text{ cm}^{-1}$ (3–5 eV), and with a long tail which extends into and even through the visible region of the spectrum. This represents a charge transfer from the ligand nonbonding levels to the $3d$ orbitals of the metal ion.

With pressure, a number of changes are observed which make a consistent picture (*I*, *2*). For high-

spin complexes, the ligand field parameter, Δ , increases by 12–15% in 150 kbar, while the Racah parameters decrease by 10–12% in the same range. The isomer shifts for these complexes decrease by 0.1–0.12 mm/sec in this range of pressure, i.e., the electron density at the iron nucleus increases by 10–15% of the difference between ordinary ferrous and ferric compounds—not an insignificant change. The charge transfer peaks shift to lower energy with increasing pressure, sometimes by as much as several thousand wave numbers in 150 kbar. If one presumes that the radial maximum of the 3d orbitals spreads with increasing pressure due to interaction with the ligands, this accounts for the decrease in B and C , since the interelectronic repulsion decreases as the electron-electron distance increases. It also explains the increased electron density at the iron nucleus, as the 3s orbitals are less shielded, and the red shift of the charge transfer peak, since the spreading of the 3d orbitals decreases their energy vis-à-vis the ligand nonbonding orbitals. More accurately, the 3d orbitals increase in energy with pressure less rapidly than do the ligand orbitals.

The Oxidation State of Iron

It has been observed in this laboratory (2–8) that ferric ion reduces to ferrous ion with increasing pressure, and that this is a reversible process, with some hysteresis. The phenomenon can be understood qualitatively in terms of the observations discussed above, plus a schematic configuration coordinate diagram (Fig. 1). Here, the ordinate is potential energy, and the abscissa is typically some vibrational mode of the system which aids electron transfer. Optical transitions are rapid compared with lattice vibrations and thus occur vertically on such a diagram, in accordance with the Franck-Condon principle. Thermal transitions are not subject to this limitation. The reduction is accomplished by transfer of an electron from a nonbonding ligand orbital to

O = OPTICAL TRANSITION
T = THERMAL TRANSITION

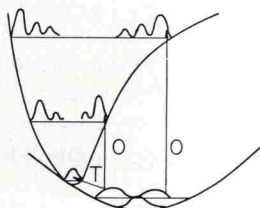


FIG. 1. Schematic configuration coordinate diagram.

the metal 3d antibonding orbital—the charge transfer process discussed above. The steep slope of the excited state potential well is consistent with the long tail observed on the optical charge transfer peak. It can be seen that the thermal transfer may involve relatively small energy, so that the observed red shift of the optical peaks is sufficient to establish a new ground state.

One would expect from the above description that complete reduction would occur over a relatively narrow pressure range—such that the excited state potential well lowers in energy by about kT with respect to the ground state. In fact, the reduction takes place continuously over a wide pressure range. For most systems the relationship between concentration and pressure can be expressed in the form,

$$K = \frac{C_{II}}{C_{III}} = AP^B, \quad (1)$$

where C_{II} and C_{III} are the concentrations (actually the *site fractions*) of ferrous and ferric sites, and A and B are constants, so that $\ln K$ is a linear function of $\ln P$. Consecutive runs at the same pressure gave the same conversions, so that the observations involved an equilibrium phenomenon, not the result of slow kinetics. The constants A and B for a variety of systems appear in Table II. Figures 2–4 show typical data. In Fig. 2 are shown FeCl_3 , FeBr_3 , and $\text{Fe}(\text{NCS})_3$. These systems have in common the fact that ligands are shared between adjacent iron ions so that there is strong coupling between sites. The slope of the line is ~ 0.5 —a relatively small value, as we shall see. Figure 3 exhibits data for two hydrates and ferric acetylacetonate. For these cases there is little or no sharing of ligands between sites, and the slope is ~ 1.0 . In

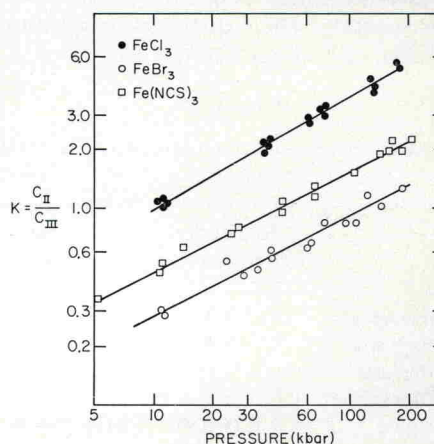


FIG. 2. $\ln K$ vs $\ln P$ —crystals with strong coupling between sites.