Table I

Constants for the Equation $K = C_{II}/C_{III} = AP^B$

Compound	A	B
$FeCl_3$	0.265	0.56
$FeBr_3$	0.076	0.43
$KFeCl_4$	0.092	0.50
$FePO_4$	0.078	0.46
Phosphate glass	0.048	0.31
Ferric acetate (418°K)	0.022	0.98
Ferric citrate	0.112	0.25
$K_3Fe(CN)_6$	0.109	2.06

$(NH_3)_6Cl_3$, $K_3Fe(CN)_6$, ferric citrate, basic ferric acetate, ferric acetylacetonate, ferric oxalate, various hydrates, hemin, and hematin.

The pressure dependence of the conversion is of the form

$$K = AP^B \tag{2}$$

where the equilibrium constant K is defined as $K = C_{II}/C_{III}$, and A and B are independent of pressure. Typical values for these constants appear in Table I, and plots are given in Figures 4 and 5 for representative compounds.

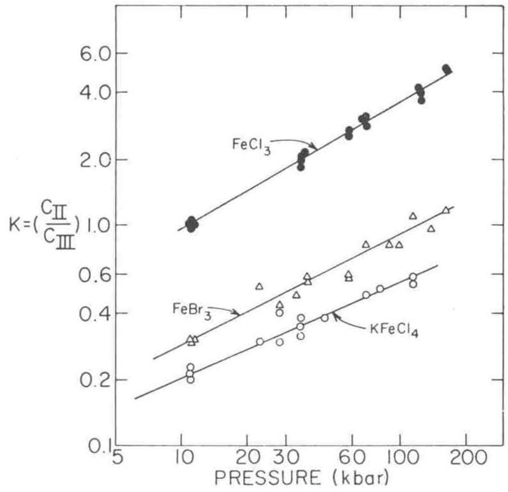

Figure 4. Ln K *vs.* ln P diagram for halides.

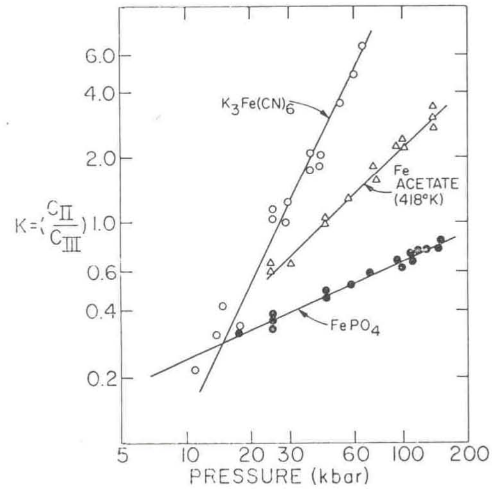

Figure 5. Ln K *vs.* ln P diagram for $FePO_4$, $K_3Fe(CN)_6$, and basic ferric acetate.

Successive spectra at the same pressure are essentially identical, while, after the pressure is changed, as soon as a spectrum is identifiable on the oscilloscope the changed conversion is evident, so it is clear that one is observing equilibrium, not the results of slow kinetics. As discussed in the papers, the concentrations measured are nominal, because of differences in $\langle x_2 \rangle$ at different sites, etc., but should be a good approximation.

For all compounds studied so far, except hemin and hematin, K increases with increasing temperature, *i.e.*, the reactive is endothermic,[9] with a heat of reaction in the range 0.1–0.5 eV which usually increases with increasing temperature. For the halides it is independent of pressure but in more covalent systems it may increase or decrease markedly with pressure.

The problems which arise are (1) why there is such a general tendency for ligand–metal electron transfer, and (2) why the pressure dependence is of the observed form, *i.e.*, why there is not a discontinuous reduction at some pressure?

As discussed in the introduction, optical transfer of an electron requires 3–5 eV. The red shift with pressure, while considerable, is not sufficient to move the optical transition to zero energy. However, the high-pressure transition observed here is a thermal effect occurring sufficiently slowly so that the coordinates can assume their new equilibrium values, whereas the optical transition must take place vertically on a configuration coordinate diagram, according to the Franck–Condon principle. The situation is illustrated schematically in Figure 6. The horizontal coordinate is typically displacement along some vibrational mode of the system (metal plus ligands) which permits the rearrangement.

The pressure dependence can be discussed as follows. When electron transfer takes place one creates a ferrous ion in a ferric site plus a radical or radical ion or possibly an excitation smeared out over several ligands. There is, thus, a charge redistribution and local compression and distortion which affect neighboring ions, distorting the potential wells so as to make electron transfer less favorable. Increased pressure lowers the excited state further, allowing more conversion which increases the strain. The hysteresis on release of pressure can be associated with stored-up strain.

A thermodynamic analysis of the situation is given by

$$K = \exp(-G/RT) \tag{3}$$

$$\frac{\partial \ln K}{\partial \ln P} = \frac{P\Delta V}{RT} = \frac{P(V^{III} - V^{II})}{RT} = B \tag{4}$$

eq 3 and 4, where V^{III} and V^{II} refer to the volumes of the sites plus their associated ligands. One can rearrange eq 4 to give eq 5. Thus the fractional increase

$$\frac{\partial \ln C_{II}}{\partial \ln P} = P\,\frac{(V^{III} - V^{II})}{RT}\,(C_{III}) \tag{5}$$

in conversion with fractional increase in pressure is proportional to the concentration of sites available to convert. The proportionality constant is the work to create a reduced site measured in thermal units (units of

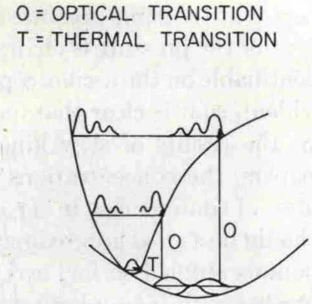

Figure 6. Schematic configuration coordinate diagram.

RT). The fact that the work is constant is surprising. From our results, it apparently applies in the pressure range 10–200 kbars. Since concentrations below 6–7% or much above 90% are very hard to measure accurately, this relationship may not be valid for dilute mixtures.

The fact that the heat of reaction varies with temperature is reasonable since possible thermal processes include promotion of electrons from ground to excited electronic state, redistribution of electrons among vibrational levels of the ground state, and possible deformation of the potential wells to retard or promote electron transfer.

Ferrocene

Ferrocene (dicyclopentadienyliron) represents an appropriate material to discuss in detail as its high molecular symmetry, D_{5h}, has made feasible a number of theoretical studies.[23–27]

Using the SCF–LCAO calculation of Dahl and Ballhausen[27] as a starting point one can account for the pressure-induced effects through ideas developed by Wolfsberg and Helmholz[28] by means of a zeroth order molecular orbital treatment.[29] Wolfsberg and Helmholz made the suggestion that in LCAO molecular orbital treatments the off-diagonal matrix elements could be treated as proportional to the overlap of the corresponding orbitals. In the case of ferrocene, one can obtain the initial matrix elements from the work of Dahl and Ballhausen and one only needs the change that will occur in each matrix element with the reduction in interatomic distance that is produced with the application of pressure. This is obtained in the spirit of the Wolfsberg and Helmholz approximation by assuming that the change produced by pressure in each matrix element is proportional to the change produced in the corresponding overlap integrals.

The precise effect of pressure on the interatomic distances in ferrocene is not known, but an estimate was obtained from force constants calculated from infrared and Raman spectra. Other high-pressure work[30] has shown the compressibility of the carbon–carbon bond to be small, and as the interest here is in metal–ligand interactions only the carbon–metal distance was assumed to change with pressure. From the published frequencies for the A_{1g} and A_{2u} ring–metal stretching frequencies,[31] a compression of about 1% in 100 kbars was predicted.

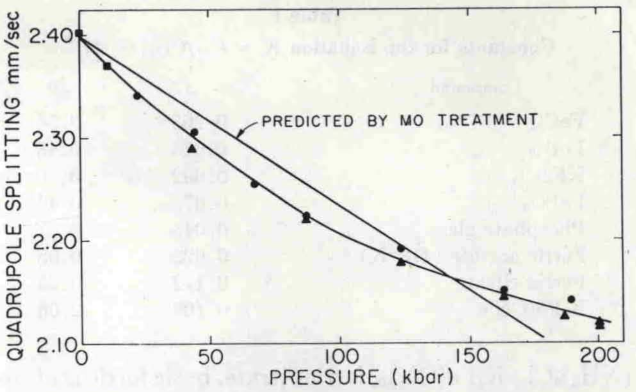

Figure 7. Quadrupole splitting *vs.* pressure diagram for ferrocene.

With this information the necessary overlap integrals were calculated, the off-diagonal elements were adjusted for the change produced in the overlap integrals, and the matrix equations were solved to give the changes in the orbital energies and coefficients of the linear combinations of atomic orbitals.[29] The changes in the electronic parameters considered here, the isomer shift, the quadrupole splitting, and the shift of the optical-absorption peak near 24,000 cm^{-1} were then extracted from these results.

First, consider the quadrupole splitting. Working within the SCF–LCAO molecular orbital description of Höfflinger and Voitländer,[32] who have examined in detail the various components of the electric-field gradient in ferrocene, and using the necessary numerical constants from their work and the calculated changes in orbital occupation with pressure, the predicted fractional change in the electric field gradient was obtained. The electric field gradient is proportional to the quadrupole splitting, and so the fractional change in the electric field gradient is plotted in Figure 7 as the fractional change in the quadrupole splitting.

The major effect comes from the change in the occupation of the d orbitals. The reduction in the ring–metal distance causes a significant flow of electrons in the e_{2g} orbitals from metal (3d ± 2) to ligand, and in the e_{1g} orbitals from ligand to metal (3d ± 1). As the electric-field gradient produced by the e_{2g} is opposite in sign to that produced by the e_{1g} orbitals, both contributions add to produce the large decrease in the quadrupole splitting experimentally observed.

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