Finally, there is a set of compounds which undergoes change of both oxidation state and spin state. These are the iron porphyrins, which consist of four pyrrole rings with methine bridges, and various substituents on the outer pyrrole carbons. In hemoglobin there are four protoporphyrin IX molecules coordinated to imidazole groups of the globin protein. High pressure studies have been made on ferric protoporphyrin derivatives: hemin and hematin, which have respectively one Cl^- or one OH^- coordinated axially to the iron; and imidazole protoheme (80), with two imidazoles in the axial positions. In hemin and hematin the iron is about 0.5 Å out of the molecular plane and is high spin. In the imidazole complex it is nearly in the plane and is low spin.

The iron reduces with pressure in all three crystals but more easily in hemin and hematin than in the imidazole complex. At room temperature the ferrous iron formed from the imidazole protoheme is in an intermediate spin or mixed spin state. At elevated temperature, where it reduces at low pressure, low spin ferrous iron is formed, which transforms to intermediate spin with increasing pressure. The increase in spin is associated with a reduction in back-donation such as discussed earlier for other systems. In hemin and hematin the high spin ferric iron apparently reduces directly to intermediate spin or mixed spin ferrous iron. The high spin state is possible only as long as the iron is well out of the molecular plane; since pressure forces the iron back towards the plane, it reduces the probability of the high spin state. The behavior of the Mössbauer parameters, in particular the large increase in the quadrupole splitting of the ferric iron, is consistent with this interpretation.

The high pressure data supplements the information obtained by changing the substituents on the periphery of the molecule and illustrates the use of pressure to increase our understanding of atmospheric pressure chemistry.

Thermal vs optical transitions.—In the low spin to high spin transition discussed above we postulated that there was significant thermal occupation of the ligand π^* orbitals by ligand π electrons at high pressure. In the reduction process we postulated that an electron was transferred thermally from a ligand nonbonding π orbital to a metal d_π orbital. Optical transitions have been observed in many of these materials from the ligand π to the π^* orbitals, and from ligand π to metal d_π orbitals. For both of these transitions ν_{max} lies in the range 2–5 eV, with the charge transfer transition somewhat the lower in energy. In both cases the peak shifts significantly to lower energy with pressure. This implies an increased probability of occupation of the "excited" state at high pressure, so that the volume of the system as a whole must be smaller after electron transfer.

However, the red shifts observed (0.2–0.7 eV in 100 kbar) are only a modest fraction of ν_{max}, while significant conversion is frequently noted by 50–75 kbar pressure. Thus, the thermal process must require considerably less

energy than the optical process. Large differences between the thermal and optical energy requirements have been observed for other systems. Color centers in alkali halides typically absorb in the region 2–4 eV. Yet they can be thermally bleached at moderate temperatures (sometimes as low as $100°K$) (81). Analogous results have been observed in a variety of chemical electron transfer processes, the theory for which has been reviewed by Marcus (82). In the special case of oxidation-reduction coupling of ions in solutions (e.g. $Fe^{+3} - Fe^{+2}$; $V^{+3} - V^{+2}$; $Cr^{+3} - Cr^{+2}$) the thermal energy is independent of which ion an electron is on ($E_{th} = 0$), yet the optical absorption gives ν_{max} in the range 2–3 eV.

There are a number of reasons for the difference in energy between optical and thermal transitions. First, optical transitions are subject to the Franck-Condon restriction, i.e. they must occur vertically on a configuration coordinate diagram while thermal transitions are not subject to this limitation (see Figure 1).

Second, in the high pressure thermal process the volume is the relevant configuration coordinate, while the optical process in general will involve more coordinates. This factor could act to increase further the difference between the optical and thermal energies.

A third factor which can increase the difference between optical and thermal transition energies is configuration interaction as illustrated in Figure 1. This is caused by partial breakdown of the Born-Oppenheimer approximation due to spin orbital coupling. The conditions have been discussed for color centers by Henry & Slichter (83) and for electron transfer processes by Marcus (82) and Hush (84). The latter author has shown that the separation between energy surfaces should increase significantly with increased orbital overlap, as would obtain at high pressure.

In the fourth place, there is the matter of selection rules. For allowed optical transitions a change in parity between states is required. In the charge transfer process the metal d_π states are of g symmetry, so the optically observed transition must be from a ligand state of u symmetry. However, for ligands with filled p orbitals the highest filled molecular orbital has t_{1g} symmetry, and the thermal transfer, which is not subject to the selection rule, will be from this orbital. Jorgenson (85) has shown that for halide ligands the energy difference between π (t_{1g}) and π (t_{1u}) is typically 0.75–1.0 eV. For the π-π^* transition on the ligand apparently, in general, no selection rule limits the optical transition from the highest filled to the lowest empty level.

A fifth factor is also operative in the case of reduction of Fe(III) to Fe(II): the crystal field stabilization energy. For the ferrous state the lowest $3d$ level is lowered in energy by 0.4Δ, where Δ is the ligand field strength. There is no corresponding shift for Fe(III).

One can make a crude estimate of the difference between optical and thermal transition energies from a relationship derived from the work of