

○ = Optical transition

T = Thermal transition

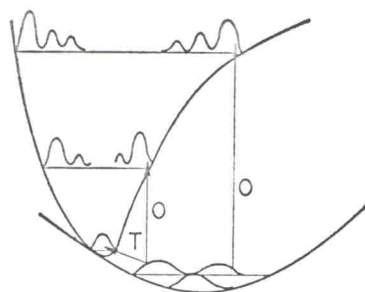


Fig. 4. Schematic configuration coordinate diagram.

heated in the dark (13). In both cases CO_2 is evolved and the process is irreversible. This high pressure process is reversible, and it is not necessary to postulate the formation of CO_2 in the lattice. Nevertheless, the radical formed on reduction may well have a partial molar volume which is quite temperature dependent.

One can obtain a heat of reaction from the relationship:

$$\frac{\partial \ln K}{\partial \frac{1}{T}} = \frac{\Delta H}{R} \quad (5)$$

Values of ΔH are listed in Table 2. In almost all cases the reaction is endothermic. (See the discussion of hemin and hematin below.) The heat of reaction generally increases with increas-

ing temperature. The pressure dependence is, of course, related to the change of B with temperature.

It is possible to give a reasonable discussion of the electron transfer process. The peaks which represent optical transfer of an electron from ligand to metal shift to lower energy with increasing pressure, as discussed earlier in the paper. However, at 10 kilobars this shift represents only a modest fraction of the total energy involved in photoexcitation of the electron. Even at 100 kilobars the shift is only $\frac{1}{3}$ to $\frac{1}{4}$ of the energy difference at 1 atmosphere. One must recognize, however, that the high pressure thermal process may require much less energy than the optical process. Fig. 4 represents a schematic configuration coordinate diagram. The horizontal coordinate is typically a vibrational displacement which aids the electron transfer. By the Franck-Condon principle, optical processes take place vertically on such a diagram. The thermal process is not subject to this restriction. The steep potential well shown for the excited state is consistent with the tail observed for the optical charge transfer peak. Thus, a relatively small vertical displacement of the excited state potential well with respect to the ground state may permit electron transfer.

When the ferric ion at a given site is reduced, a free radical is produced at a ligand site (or a hole may be smeared

out over several ligands). This involves a displacement of charge as well as, quite probably, a physical distortion of the lattice. The combination of strain and electric polarization operating on the neighboring sites distorts the potential wells and reduces the probability of reduction. Further pressure increase lowers the energy of the excited state further and increases the amount of reduction, but at the expense of further strain. These factors must balance out to give the linear relationship observed experimentally. Since $\bar{V}^{\text{III}} - \bar{V}^{\text{II}}$ is positive (Eq. 2) while the Fe(III) ion is smaller than the Fe(II) , there must be a considerable contraction of ligand volume on formation of the free radical.

There are several types of thermal processes involved; the transfer of electrons from ground to excited state, the redistribution in the vibrational levels, and the possible effect of temperature in modifying the shape of the potential wells to relieve or intensify strain. It is not surprising that the heat of reaction is generally dependent on both temperature and pressure. The reduction process is reversible, but frequently involves more or less hysteresis, which can be associated with the mechanical and electrical strains stored in the lattice during the process.

V. Special Cases

In this section we discuss three groups of compounds each of which has aspects of particular interest. In Fig. 5 are presented conversion data for $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$, and $\text{FeCl}_3 \cdot 6\text{NH}_3$ (7). For $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ it is well established (14) that the iron has four H_2O ligands and two Cl^- ligands. The structures of the other two are not so well resolved, but it is quite certain that they involve some, if not all, molecular ligands. It is seen that the ligand-to-metal electron transfer takes place with these compounds also. The conversion for $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is of the same order as that for the anhydrous material but the value of B (and hence of $\Delta\bar{V}$) is almost twice as large (see Table 1). The $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ exhibits the same value of B (same $\Delta\bar{V}$) as the hydrated chloride, but a smaller value of A . This compound proved to be very sensitive to H_2O content. The results reported here are for material equilibrated for five months over a saturated CaCl_2 solution. It gave both the correct x-ray pattern and the precise chemical

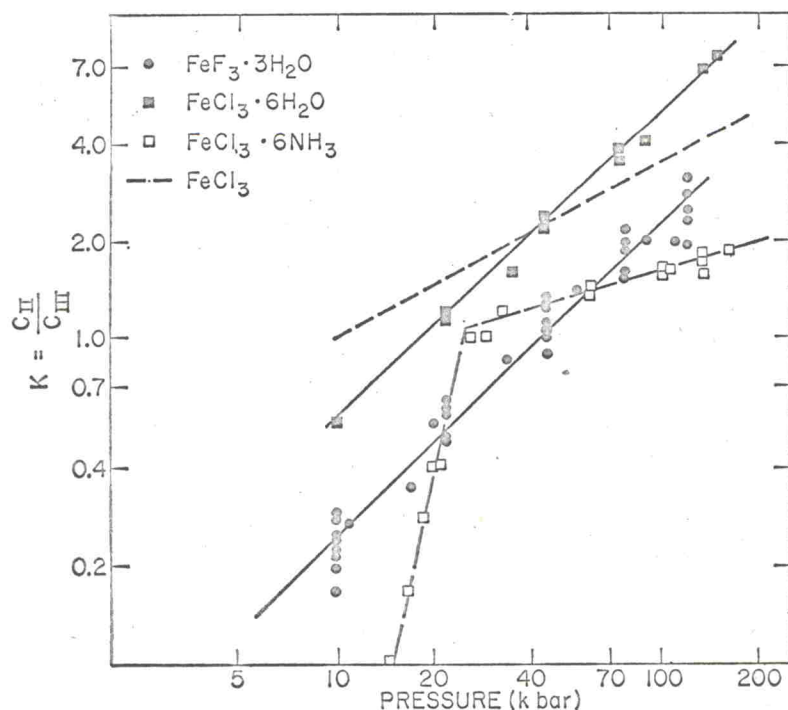


Fig. 5. $\ln K$ vs. $\ln P$ — $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{NH}_3$, and $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$