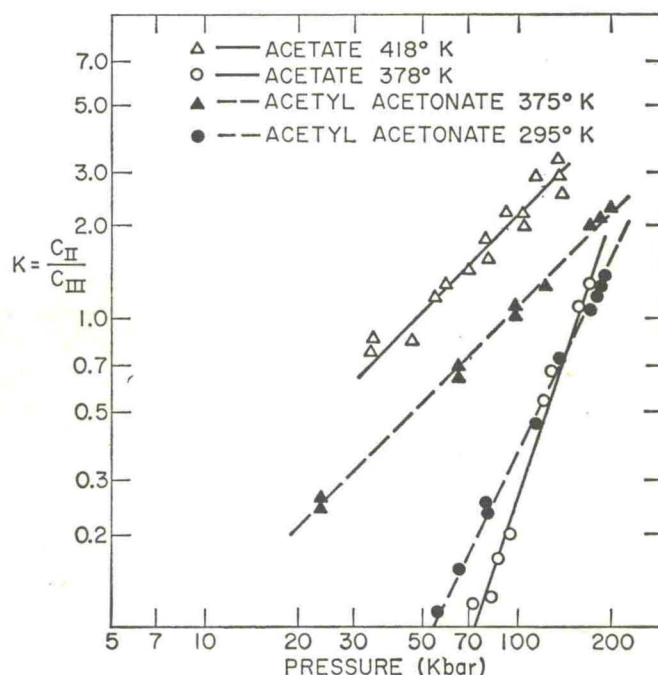Fig. 2. ln $K$ vs. ln $P$—Ferric halides



Fig. 3. ln $K$ vs. ln $P$—Acetylacetonate and basic acetate.

much over 90% are difficult to establish accurately, so one cannot say whether this description is applicable at very high dilution. For the halides, as well as for several other compounds which can be classified as relatively ionic, $B \cong 0.5$ with little temperature dependence. This corresponds to values of $\Delta\overline{V}$ which range from about 1.2 cc at 10 kilobars to about 0.06 cc at 200

Table 1. Constants $A$ and $B$ for the relationship $K = AP^B$.

| Material | Temperature (°K) | $A$ | $B$ |
|---|---|---|---|
| FeCl₃ | 295 | 0.265 | 0.564 |
| FeBr₃ | 295 | 0.076 | 0.426 |
| KFeCl₄ | 295 | 0.091 | 0.497 |
| FePO₄ | 295 | 0.079 | 0.457 |
| Fe Citrate | 295 | 0.112 | 0.350 |
| K₃Fe(CN)₆ | 295 | 0.109 | 2.06 |
| Fe acetylacetonate | 295 | $1.2 \times 10^{-5}$ | 2.23 |
| Fe acetylacetonate | 375 | $0.96 \times 10^{-2}$ | 1.01 |
| Fe basic acetate | 378 | $0.22 \times 10^{-6}$ | 3.05 |
| Fe basic acetate | 418 | $2.21 \times 10^{-2}$ | 0.98 |
| Fe oxalate | 295 | 0.041 | 0.51 |
| Fe oxalate | 335 | 0.029 | 0.83 |
| Fe oxalate | 383 | 0.043 | 1.146 |
| Strontium Fe oxalate | 295 | 0.115 | 0.301 |
| Strontium Fe oxalate | 383 | 0.058 | 0.844 |
| FeCl₃ • 6H₂O | 294 | 0.063 | 0.95 |
| FeF₃ • 3H₂O | 294 | 0.027 | 0.95 |
| FeF₃ • 3H₂O plus excess H₂O | 294 | 0.072 | 0.95 |
| FeCl₃ • 6NH₃ < 25 kbar | 294 | $2.4 \times 10^{-6}$ | 4.06 |
| FeCl₃ • 6NH₃ > 25 kbar | 294 | 0.46 | 0.27 |
| Fe(NCS)₃ • 6H₂O | 295 | 0.136 | 0.528 |
| K₃Fe(NCS)₆ | 295 | 0.024 | 0.692 |
| Hemin | 294 | $5.5 \times 10^{-3}$ | 1.53 |
| Hemin | 335 | $4.2 \times 10^{-4}$ | 2.04 |
| Hemin | 367 | $3.5 \times 10^{-5}$ | 2.57 |
| Hematin | 294 | $2.7 \times 10^{-5}$ | 2.67 |
| Hematin | 343 | $1.4 \times 10^{-7}$ | 3.77 |

kilobars. As discussed later, the conversion introduces stresses in the neighborhood of the reduced site. One can insert a term of the form

$$-\Sigma \varepsilon_i d\sigma_i$$

in the free energy, where $\varepsilon$ and $\sigma$ refer to strains and stresses introduced by the reduction. Then the $\Delta V$ of Eq. 2 can be written:

$$\Delta\overline{V} = \Delta V' - \sum_i \varepsilon_i \frac{\partial \sigma_i}{\partial p} \quad (4a)$$

or, in the language of solution theory:

$$\Delta\overline{V} = \Delta V' - \frac{\partial V_e}{\partial C_{II}} \quad (4b)$$

where $\Delta V'$ is the difference in unstrained volumes of the ferric and the ferrous site, and $V_e$ is the excess volume of mixing. Since $V_e$ is strongly concentration dependent, and the concentration of ferrous sites varies with pressure as discussed above, one can understand why $\Delta V$ varies with pressure. It can be shown that a small value of $B$ implies a large negative value of

$$\frac{\partial V_e}{\partial C_{II}}$$

at low concentration of ferrous sites (low pressure), and strong coupling between adjacent sites, whereas large $B$ implies weak coupling between adjacent ions or molecules.

Fig. 3 exhibits conversion data for the basic acetate and acetylacetonate

(4). Both of these ligands are bidentate with each molecule attaching to the iron through two oxygens. The values of $B$, and hence of $\Delta\overline{V}$, are significantly larger here than for the halides, and decrease measurably with increasing temperature. On the other hand, ferric oxalate and strontium ferric oxalate (4) [Sr₃(Fe(C₂O₄)₃)₂•2H₂O] also have bidentate ligands attached through oxygen, but both show an increase of $\Delta\overline{V}$ with temperature (Table 1). It is known that the oxalates reduce photochemically at 1 atmosphere (11, 12) and undergo a series of reactions when

Table 2. Heats of reaction.

| Material | Pressure (kbar) | Temperature (°K) | $\Delta H$(eV) |
|---|---|---|---|
| FeCl₃ | * | 323 | 0.12 |
| FeCl₃ | * | 393 | 0.18 |
| FeBr₃ | * | 323 | 0.20 |
| FeBr₃ | * | 393 | 0.32 |
| KFeCl₄ | * | 323 – 393 | 0.07 |
| Fe acetylacetonate | 60 | 325 | 0.15 |
| Fe acetylacetonate | 60 | 375 | 0.25 |
| Fe acetylacetonate | 150 | 325 | 0.065 |
| Fe acetylacetonate | 150 | 375 | 0.085 |
| Fe basic acetate | 75 | 398 | 0.93 |
| Fe basic acetate | 150 | 398 | 0.44 |
| Fe oxalate | 25 | 315 | 0.19 |
| Fe oxalate | 25 | 360 | 0.34 |
| Fe oxalate | 100 | 315 | 0.26 |
| Fe oxalate | 100 | 360 | 0.42 |
| Strontium Fe oxalate | 20 | 333 | 0.11 |
| Strontium Fe oxalate | 200 | 333 | 0.24 |
| Hemin | 20 | 335 | − 0.22 |
| Hemin | 60 | 335 | − 0.11 |
| Hemin | 90 | 335 | − 0.057 |
| Hematin | 40 | 320 | − 0.23 |
| Hematin | 90 | 320 | − 0.052 |

* Independent of pressure
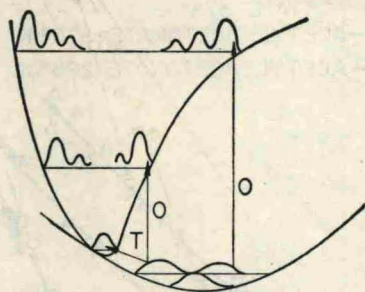
O = Optical transition

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 $\Delta H$ 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 ⅓ to ¼ 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 $\overline{V}^{III} - \overline{V}^{II}$ 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 $FeCl_3 \cdot 6H_2O$, $FeF_3 \cdot 3H_2O$, and $FeCl_3 \cdot 6NH_3$ (7). For $FeCl_3 \cdot 6H_2O$ 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 $FeCl_3 \cdot 6H_2O$ is of the same order as that for the anhydrous material but the value of $B$ (and hence of $\Delta \overline{V}$) is almost twice as large (see Table 1). The $FeF_3 \cdot 3H_2O$ exhibits the same value of $B$ (same $\Delta \overline{V}$) 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
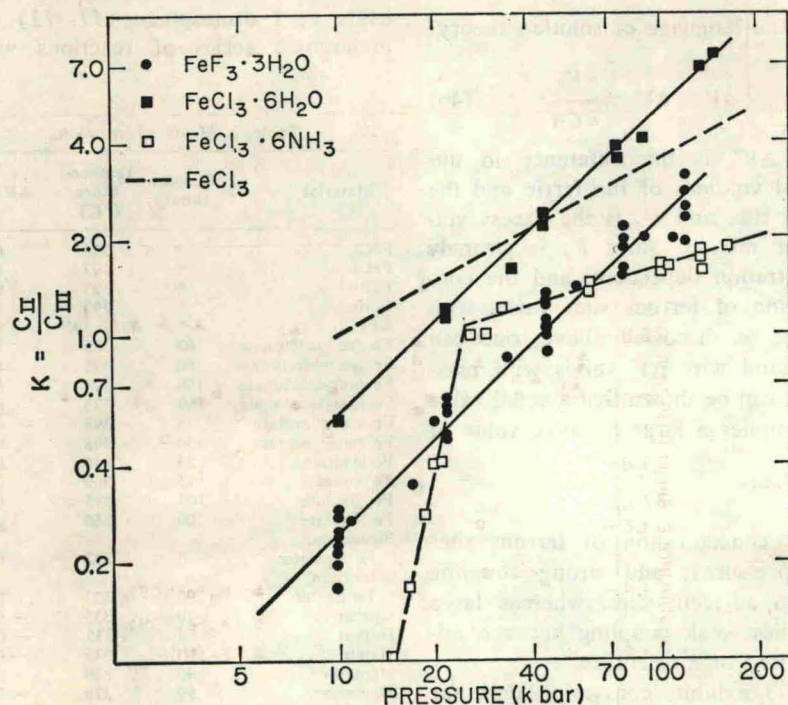


Fig. 5. ln $K$ vs. ln $P$—FeCl₃·6H₂O, FeCl₃·6NH₃, and FeF₃·3H₂O