

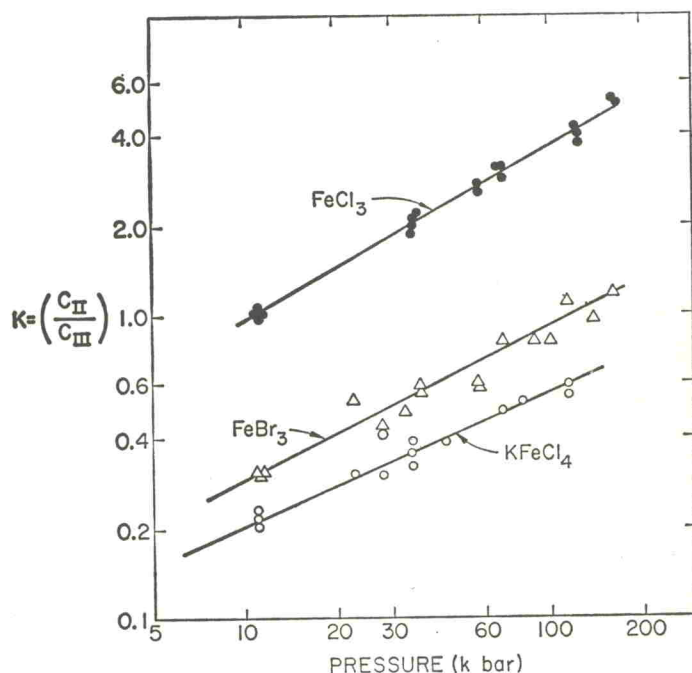


Fig. 2. $\ln K$ vs. $\ln P$ —Ferric halides

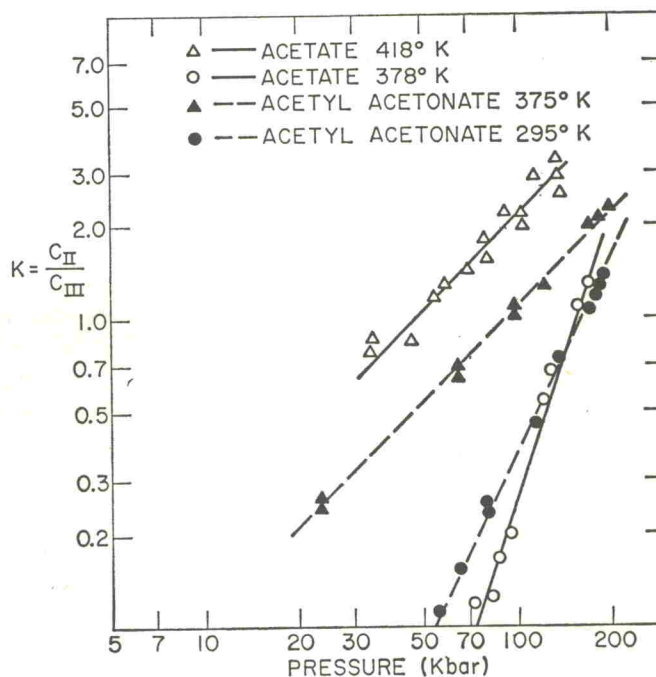


Fig. 3. $\ln K$ vs. $\ln P$ —Acetylacetonate and basic acetate.

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, $B \approx 0.5$ with little temperature dependence. This corresponds to values of $\Delta \bar{V}$ which range from about 1.2 cc at 10 kilobars to about 0.06 cc at 200

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

$$-\sum \epsilon_i d\sigma_i$$

in the free energy, where ϵ and σ refer to strains and stresses introduced by the reduction. Then the ΔV of Eq. 2 can be written:

$$\Delta \bar{V} = \Delta V' - \sum \epsilon_i \frac{\partial \sigma_i}{\partial p} \quad (4a)$$

or, in the language of solution theory:

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

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 $\Delta \bar{V}$ 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 $\Delta \bar{V}$, 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) $[\text{Sr}_3(\text{Fe}(\text{C}_2\text{O}_4)_3)_2 \cdot 2\text{H}_2\text{O}]$ also have bidentate ligands attached through oxygen, but both show an increase of $\Delta \bar{V}$ 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 1. Constants A and B for the relationship $K = AP^B$.

Material	Temperature (°K)	A	B
FeCl ₃	295	0.265	0.564
FeBr ₃	295	0.076	0.426
KFeCl ₄	295	0.091	0.497
FePO ₄	295	0.079	0.457
Fe Citrate	295	0.112	0.350
K ₂ Fe(CN) ₆	295	0.109	2.06
Fe acetylacetonate	295	1.2×10^{-5}	2.23
Fe acetylacetonate	375	0.96×10^{-2}	1.01
Fe basic acetate	378	0.22×10^{-6}	3.05
Fe basic acetate	418	2.21×10^{-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
FeCl ₃ · 6H ₂ O	294	0.063	0.95
FeF ₃ · 3H ₂ O	294	0.027	0.95
FeF ₃ · 3H ₂ O plus excess H ₂ O	294	0.072	0.95
FeCl ₃ · 6NH ₃ < 25 kbar	294	2.4×10^{-6}	4.06
FeCl ₃ · 6NH ₃ > 25 kbar	294	0.46	0.27
Fe(NCS) ₃ · 6H ₂ O	295	0.136	0.528
K ₂ Fe(NCS) ₆	295	0.024	0.692
Hemin	294	5.5×10^{-3}	1.53
Hemin	335	4.2×10^{-4}	2.04
Hemin	367	3.5×10^{-5}	2.57
Hematin	294	2.7×10^{-5}	2.67
Hematin	343	1.4×10^{-7}	3.77

Table 2. Heats of reaction.

Material	Pressure (kbar)	Temperature (°K)	ΔH (eV)
FeCl ₃	*	323	0.12
FeCl ₃	*	393	0.18
FeBr ₃	*	323	0.20
FeBr ₃	*	393	0.32
KFeCl ₄	*	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

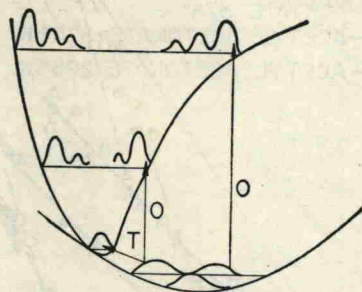


Fig. 4. Schematic configuration coordinate diagram.

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 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

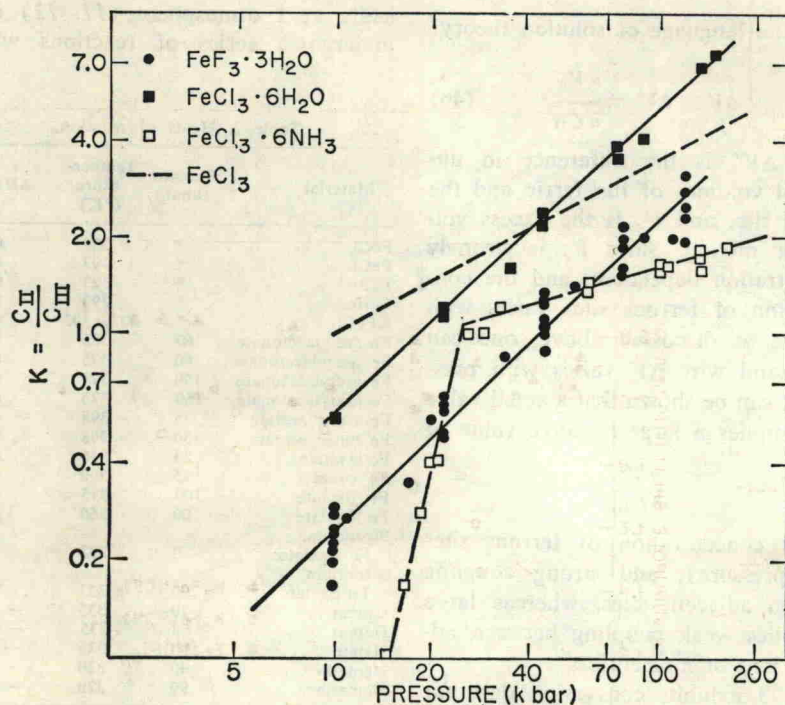


Fig. 5. $\ln K$ vs. $\ln P$ — $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{NH}_3$, and $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$