TABLE II

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
$K_3Fe(CN)_6$	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
$FeCl_3 \cdot 6H_2O$	294	0.063	0.95
$FeF_3 \cdot 3H_2O$	294	0.027	0.95
$FeF_3 \cdot 3H_2O$ plus excess H_2O	294	0.072	0.95
$FeCl_3 \cdot 6NH_3 < 25$ kbar	294	2.4×10^{-6}	4.06
$FeCl_3 \cdot 6NH_3 > 25$ kbar	294	0.46	0.27
$Fe(NCS)_3 \cdot 6H_2O$	295	0.136	0.528
$K_3Fe(NCS)_6$	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

Fig. 4 are shown conversion data for hemin and hematin. These are prototype molecules for hemoglobin, and thus are of biological interest. They form molecular crystals with very little coupling between sites. The slope B is in the range 2.5–3.0. From these results one can get a qualitative understanding of the pressure dependence of the conversion. When an Fe(III) ion on a given site is reduced,

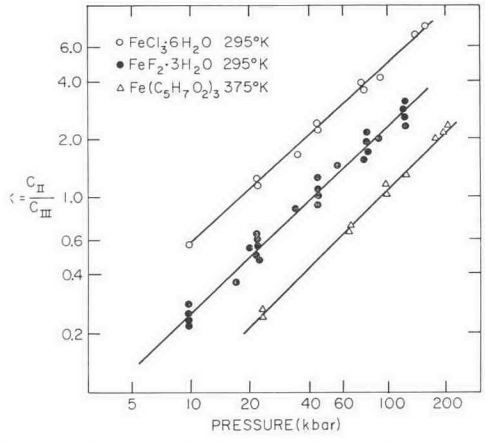

FIG. 3. ln K vs ln P—Crystals with moderate coupling between sites.

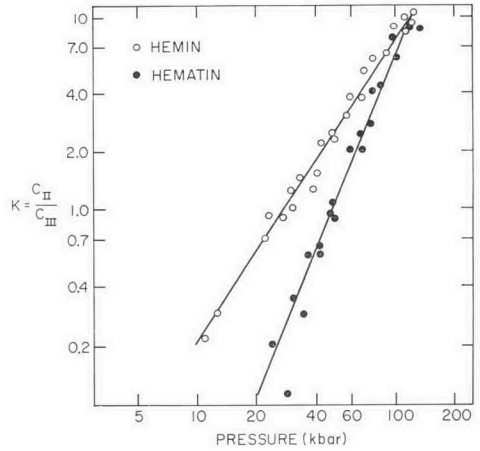

FIG. 4. ln K vs ln P—Crystals with weak coupling between sites.

an electrical polarization, and possibly a mechanical strain is introduced. This perturbs the potential wells at neighboring sites and makes the conversion of these sites more difficult. The greater the coupling between sites, the stronger this interaction and the lower the slope of the ln K vs ln P curve. Those systems with the most coupling between sites show the most hysteresis on release of pressure. In all cases, when the sample is powdered, it returns completely to the ferric state.

A simple thermodynamic analysis may be helpful in visualizing the interaction between sites in macroscopic terms. The equilibrium constant defined above can be written

$$K = e^{-\Delta \bar{G}/RT}; \tag{2}$$

then

$$\frac{\partial \ln K}{\partial \ln P} = B = -\frac{P \Delta \bar{V}}{RT}, \tag{3}$$

where $\Delta \bar{V}$ is the difference in partial molar volume of products and reactants. A rearrangement of (3) gives

$$\frac{\partial \ln C_{II}}{\partial \ln P} = \frac{P(\bar{V}_{III} - \bar{V}_{II})}{RT} C_{III}. \tag{4}$$

Thus, the fractional increase in sites converted for a given fractional increase in pressure is proportional to the fraction of unconverted sites. The coefficient of proportionality is the work to convert a site, measured in thermal units, i.e., units of RT. Over the range of concentration observable (8–92%) and in the pressure ranges 5–200 kbar, within our accuracy, this work is independent of concentration or pressure. It should be pointed out that not all systems gave the strictly linear relationship between ln K and ln P. Further, the concentrations used in this work were obtained by computer fitting Lorentzian curves to the data. In addition to the errors inherent in this process, there is a definite possibility that the f number at a converted site is different, or has a different pressure dependence, than that for a ferric site. Nevertheless, it is clear that for the vast majority of systems $\Delta \bar{V}$ must be a strong function of pressure, or of concentration. One can express this in two different ways. As indicated earlier, when a site converts, a free radical is formed at a ligand site, or a hole circulates among the adjacent ligands. There results a mechanical strain and a corresponding stress. One can insert into $d\bar{G}$ terms of the form $-\sum_i \epsilon_i d\sigma_i$, where ϵ_i and σ_i are the strains and stresses. Then

$$\Delta \bar{V} = \Delta V_0 - \sum_i \epsilon_i \frac{\partial \sigma_i}{\partial P}, \tag{5}$$

where ΔV_0 is the difference in volume of *pure* ferric and converted material—presumably a small number, and in any case, a constant. Alternatively, one can employ the language of solution theory. Using the standard analysis,

$$\Delta \bar{V} = \Delta V_0 - \frac{\partial V_e}{\partial C_{II}}, \tag{6}$$

where V_e is the excess volume of mixing. If one inserts typical data into (6), one finds that V_e is strongly dependent on concentration (or pressure), especially at low conversions, for those systems with strong coupling between sites. For systems like hemin and hematin with very weak coupling between sites, V_e varies little with concentration. In the limit of zero coupling, V_e would be identically zero for all concentrations and pressures, and the transformation would be complete in an extremely narrow range of pressure.

Heats of reaction have been obtained both by comparing points along different isotherms and from data taken along isobars. Typical values are given in Table III. For almost all systems studied, the reaction is endothermic, i.e., the yield increases

TABLE III

HEATS OF REACTION

Material	Pressure (kbar)	Temperature °K	H(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.