

THE EFFECT OF PRESSURE ON THE OXIDATION STATE OF IRON,
III. HEMIN AND HEMATIN*

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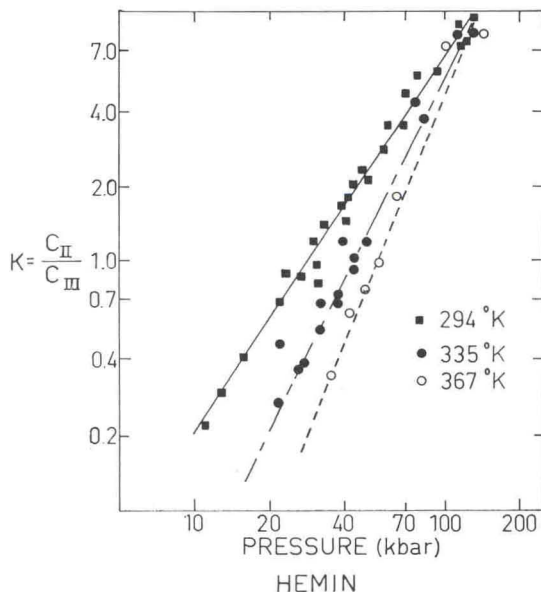
Communicated August 29, 1968

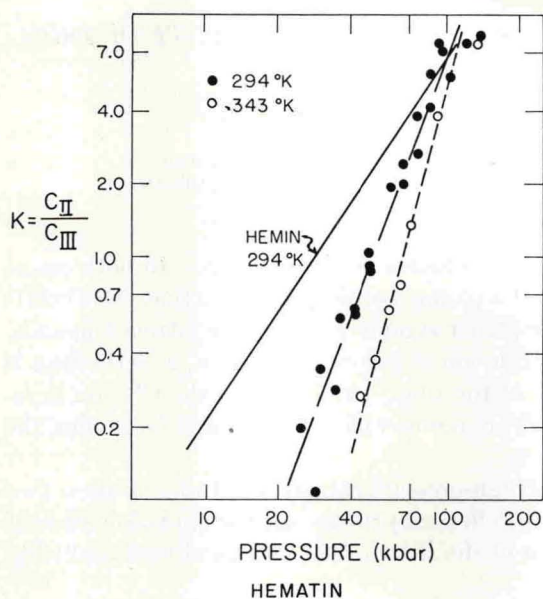
Hemin and hematin are prototype molecules for hemoglobin. In both cases, ferric iron is inserted at the center of a planar porphyrin ring so that the Fe(III) ion is in a site of essentially square planar symmetry with four nitrogen ligands. In hemin, however, there is a chloride ion attached to the iron, and the iron is displaced 0.475 Å out of the plane of the ring.¹ In hematin, the Cl⁻ ion is replaced by OH⁻; although the details are not as well determined as for hemin, the symmetry is very similar.

This paper presents the results of high-pressure Mössbauer studies of these two compounds. The emphasis is on the effect of pressure on the oxidation state of iron, although the unusual behavior of the isomer shift and quadrupole splitting of the ferric ion is also discussed.

In a previous communication,² we presented some rather qualitative results on ordinary hemin. In this work, we synthesized hemin and hematin enriched to 85 per cent in Fe⁵⁷. The hemin was made by the method of Moss,³ whereas hematin was obtained from the hemin by the technique of Fischer *et al.*⁴ The compounds were analyzed chemically, and optical spectra that showed the characteristic visible spectra were taken.⁵

In a series of studies^{2, 6-9} we showed that in many compounds, ferric ion reduces to the ferrous state with increasing pressure, that this is a reversible process,

FIG. 1.—Ln K vs. ln P in hemin.

FIG. 2.— $\ln K$ vs. $\ln P$ in hematin.

and that the dependence of the equilibrium on pressure is of the form $K = C_{II}/C_{III} = AP^B$. Figures 1 and 2 show that this description also applies to hemin and hematin. The constants A and B are given in Table 1. For more ionic materials such as the halides or phosphate, $B \cong 0.5$. From thermodynamic arguments,

$$\frac{\partial \ln C_{II}}{\partial \ln P} = \frac{P(V^{III} - V^{II})}{RT} (C_{III}) = B(C_{III}), \quad (1)$$

so that B is directly related to the difference in volume between the normal ferric ion with its ligands and the ferrous ion with associated (electron-deficient) ligands. The local distortion accompanying reduction is apparently considerably larger for more covalently bonded iron, as in the compounds under discussion here.

In a previous analysis,⁸ we showed that the electron transfer is from a ligand nonbonding level to a predominantly metal antibonding level. This charge transfer can frequently be observed optically and shifts to lower energy with increasing pressure. The high-pressure reduction is a thermal process and thus need not follow the Franck-Condon principle which demands that it occur verti-

TABLE 1. Constants A and B for $K = AP^B$.

Compound	A	B
Hemin		
294°K	5.5×10^{-8}	1.53
335°K	4.2×10^{-4}	2.04
367°K	3.5×10^{-5}	2.57
Hematin		
294°K	2.7×10^{-5}	2.67
343°K	1.4×10^{-7}	3.77