cally on a configuration coordinate diagram,[8] so that it involves much less energy than the corresponding optical process.

The optical charge transfer spectra of hemin and hematin are distinctly different.[5] As can be seen from Figures 1 and 2 and Table 1, the pressure at which significant reduction appears, and the values of B (or of $(V^{III} - V^{II})$) are different in the two compounds. There is thus a strong inference that the electron transfer involves the ion (chloride or hydroxide) that is out of the plane of the molecule more than the four nitrogens in the plane. The large value of $(V^{III} - V^{II})$ is more reasonable in this case also. There is, of course, the possibility of interaction between the "external" ion and the ring through the iron.

The pressure-induced reduction of Fe(III) is an endothermic process in all the compounds previously studied. This can reasonably be explained, as one is concerned with the thermally induced transfer of electrons from the ground to the excited electron state, and the usual Boltzmann factor $\exp(-E/kT)$ would give an increased conversion with increasing temperature. Figures 1 and 2 show that the reduction of hemin and of hematin is an exothermic process. An isobar confirmed the fact that the reduction did, indeed, decrease with increasing temperature. Heats of reaction are listed in Table 2; they decreased rapidly with increas-

TABLE 2. *Heats of reaction.*

Pressure (kb)	ΔH (ev)	
	Hemin	Hematin
20	0.22	—
40	0.15	0.23
60	0.11	0.15
80	0.075	0.10
90	0.057	0.052

ing pressure. The apparent explanation is that increased temperature tends to deform the potential wells so that E increases more rapidly than T. As the pressure increases, the distorting effect of higher temperatures becomes much smaller.

The primary purpose of this study was the investigation of the oxidation state of iron in hemin and hematin, as discussed above. In the course of the investigation, interesting data were accumulated on the effect of pressure on the isomer shift (s-electron density of the nucleus) and quadrupole splitting (interaction between the nuclear quadrupole moment and an electric field gradient at the nucleus) of the ferric ion in these compounds. The results are shown in Figures 3 and 4. The isomer shifts are given relative to metallic iron at one atmosphere. Our results for atmospheric isomer shift agree closely with those of Bearden *et al.*,[10] although our initial quadrupole splitting is smaller than theirs. There are some quantitative differences between hemin and hematin, but the results are so similar that only a single discussion is necessary. The dotted lines represent the qualitative results for hemin obtained on the unenriched compounds.[2]

For most compounds, a monotonic decrease in the isomer shift amounting typically to 0.08–0.12 mm/second in 150 kb is observed with increasing pressure (i.e., an increase of electron density at the nucleus). This can be associated
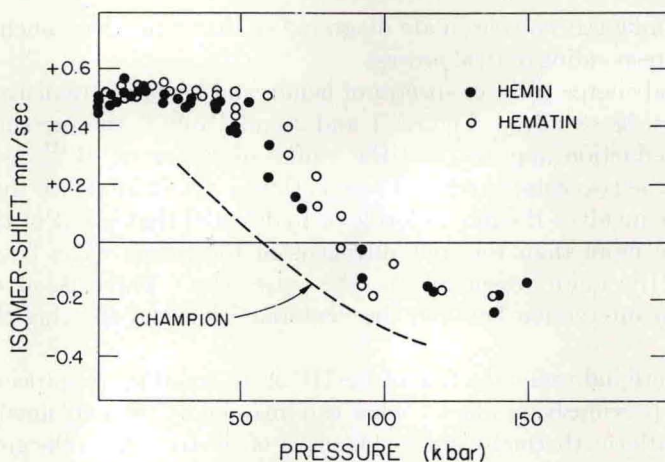
Fig. 3.—Isomer shift vs. pressure for Fe(III) ion in hemin and
hematin.

with orbital distortion effects, for example, spreading of the $3d$-orbitals due to interaction with the ligands which reduces the shielding of the $3s$-orbitals, and compression of the s-orbitals.[11] The ferric quadrupole moment almost always increases with pressure, since it is due to the field imposed by the ligands at the nucleus, which increases essentially as $1/r^3$, where r is a metal-ligand distance. For hemin, Moss[3] has obtained the following expression for the electric field gradient:

$$V_{zz} = \frac{-q_r \left| r_r{}^2 - 2z_r{}^2 \right|}{\left| r_r{}^2 + z_r{}^2 \right|^{5/2}} + \frac{2q_1}{z_1{}^3}, \tag{2}$$

where q_1 is the charge on the chloride and q_r the charge on the ring, z_1 the iron-chloride distance, z_r the distance of the iron above the ring, and r_r the effective charge radius of the ring. As discussed in a previous paper,[2] there are reasons for assuming that the electric field gradient is positive.

From Figure 3, we see that the isomer shift at first increases slightly with pressure (i.e., the electron density at the nucleus decreases); in the region of 20–40 kb a maximum is observed, and at higher pressures there is a very large decrease in isomer shift, which amounts to 0.8 mm/second in 100 kb. The quadrupole splitting increases considerably in the low-pressure region, passes through a maximum, and then decreases rapidly. Within our ability to fit the data with Lorentzian peaks, it is zero at the highest pressures.

On the one hand, it must be kept in mind that we are looking at the *ferric* ion isomer shift and quadrupole splitting—these are *unconverted* molecules; on the other hand, the maximum in the isomer shift and quadrupole splitting occur in the same pressure range and at a pressure where a significant fraction of the molecules are reduced. Furthermore, all these events occur at a measurably higher pressure in hematin than in hemin. The probability is very high that they are related.