

TABLE VI. Quadrupole splittings in high pressure products from prussian blue.

Material	Pressure (kbar)					
	25	50	100	150	175	
Low-spin Fe(III)	1.20	1.25	1.42	1.60	1.67	(23-110-147°C)
High-spin Fe(II)	...	2.00	2.1	2.10	2.10	(23°C)
	...	1.78	1.90	1.92	1.95	(110-147°C)

tion of high-spin Fe(III) to high-spin Fe(II) could be fit by the equation

$$K = C_{II}/C_{III} = 1.98 \times 10^{-3} P^{1.12} \quad (2)$$

### PRUSSIAN BLUE

The structure of prussian blue has been elucidated by Robin.<sup>17</sup> Insoluble prussian blue has the formula  $Fe_4[Fe(CN)_6]_3$ , it is a ferric ferrocyanide. A low-spin Fe(II) is coordinated to the carbon, and a high-spin Fe(III) to the nitrogen. It offers the possibility of combining ordinary ferrocyanide with a ferric salt enriched to 90% in  $^{57}Fe$ , and also of using an ordinary (2%  $^{57}Fe$ ) ferric salt with enriched ferrocyanide. Both these possibilities were exploited. The initial isomer shifts appear in Table III. Figure 10 shows spectra of  $^{57}Fe_4[Fe(CN)_6]_3$  at atmosphere and at high pressure. There is a large decrease in high-spin Fe(III) and a large increase in high-spin Fe(II). The disappearance of the Fe(III) involves both direct reduction and the electron-transfer process described below. Conversions appear in Table V.

There was no sign of low-spin Fe(III) in the spectrum. This makes isomerization (reversal of the CN<sup>-</sup> ion) very unlikely as an explanation of the low-spin to high-spin transformation

In the spectra of  $Fe_4[Fe^{57}(CN)_6]_3$  two features appear. (See Fig. 11.) At low pressure and low temperature a low-spin Fe(III) spectrum appears and grows with pressure at first. This indicates an electron transfer from the Fe(III) cation to the ferrocyanide. As can be seen from the dashed curve of Fig. 12, this equilibration is independent of temperature. Robin

<sup>17</sup> M. B. Robin, *Inorg. Chem.* **1**, 337 (1962).

and Day<sup>18</sup> have given a thorough discussion of mixed-valence compounds and electron transfer. It is of interest that the probability that the electron will appear on the iron bonded to the carbon decreases with pressure. At higher pressures, the conversion to Fe(II) high spin begins to dominate. As can be seen from Fig. 12, this conversion increases markedly with increasing temperature. The high-spin Fe(II) comes in part from the process described earlier in this paper, but at the highest pressures there is actually a reduction in the amount of Fe(III) low spin present. Figure 13 and 14 show the change in isomer shift with pressure for the low-spin Fe(II) and the low-spin Fe(III) formed by electron exchange. The Fe(II) shows a maximum at low pressure consistent with a large decrease in back donation. It should be kept in mind that the isomer shifts at elevated temperature should contain a small correction since source and absorber were at slightly different temperature. This would in no way affect the conclusions. Table VI exhibits the quadrupole splittings of the low-spin Fe(III) and high-spin Fe(II) produced under pressure.

This work reinforces the earlier work on the reduction of iron with pressure in illustrating the increase of affinity of iron for electrons with increasing compression.

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<sup>18</sup> M. B. Robin and P. Day, *Advan Inorg. Chem. Radiochem.* **10**, 247 (1967).