

TABLE 1. Isomer shift vs. pressure.*

Pressure (kb)	Fe(NCS) ₂		K ₂ Fe(NCS) ₄		K ₂ Fe(SCN) ₄	
	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)
0	0.40	—	0.39	—	0.36	0.88 (10)
25	0.36	1.34	0.37	1.33	0.34	0.94
50	0.33	1.31	0.36	1.31	0.325	1.05
75	0.31	1.29	0.35	1.30	0.315	1.15
100	0.295	1.28	0.34	1.29	0.310	1.16
125	0.28	1.27	0.33	1.28	0.300	1.18
150	0.27	1.26	0.325	1.275	—	—
175	0.26	1.25	0.32	1.27	—	—

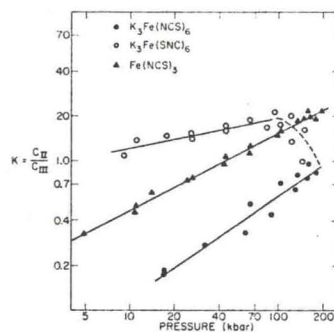
* mm/sec relative to iron metal at one atmosphere.

TABLE 2. Quadrupole splitting vs. pressure (mm/sec).

Pressure (kb)	Fe(NCS) ₂		K ₂ Fe(NCS) ₄		K ₂ Fe(SCN) ₄	
	Fe(III)	Fe(II)	Fe(III)	Fe(II)	Fe(III)	Fe(II)
0	0.58	—	0.82	—	0.82	1.15 (10)
25	0.88	2.08	0.92	2.02	0.92	1.35
50	1.05	2.14	0.99	2.00	0.99	1.60
75	1.14	2.17	1.04	2.00	1.04	1.74
100	1.19	2.20	1.09	2.00	1.09	1.84
125	1.22	2.22	1.12	2.00	1.12	1.90
150	1.24	2.24	1.15	2.00	—	—
175	1.25	2.26	1.17	2.00	—	—

The infrared spectrum of K₂Fe(SCN)₄ exhibited a rather sharp peak near 2100 cm⁻¹, which would indicate the probability of thiocyanate bonding. The atmospheric Mössbauer spectrum showed a pair of asymmetric peaks at slightly lower isomer shift (slightly higher electron density) than the Fe(NCS)₂·6H₂O. With the application of 10 kb pressure, a pair of new peaks appeared with an isomer shift of about 0.9 mm/sec and a quadrupole splitting of 1.1 mm/sec. This isomer shift is in the range observed for compounds like FeS, FeSe, and FeTe. The material was about half converted at 10 kb, and the conversion increased slowly with pressure (*open circles*, Fig. 1). Meanwhile, the isomer shift and quadrupole splitting of the new peaks increased rapidly with increasing pressure, as can be seen in Figures 2 and 3. The peaks did not broaden, so that apparently there was a single ferrous material, not a mixture. Above 100 kb the conversion actually decreased with increasing pressure, as can be seen in Figure 1. Upon release of pressure the conversion reversed, and we found only a pair of symmetric peaks much like those found for Fe(NCS)₂·6H₂O. Since our samples were considerably diluted with boron, it was difficult to get a good optical spectrum after a pressure run, but it appeared that the C-N stretching peak was shifted to lower frequency, and probably broadened.

If a sample that had been at high pressure was powdered and reloaded, it exhibited two symmetric peaks at slightly higher isomer shift (lower electron density) than the original material but in the range of typical ferric compounds (see Table 1). As can be seen in Figure 1, the material converted to the ferrous state with increasing pressure (*solid circles*) but with a much smaller conversion at a given pressure, in the low-pressure region. However, by 140–160 kb, the

Fig. 1. $\ln K$ vs. $\ln P$ vs. Fe(NCS)₂·6H₂O, K₂Fe(SCN)₆, and K₂Fe(NCS)₆.

conversion was essentially the same as in the original material compressed to this pressure. Upon release of pressure the ferrous peaks disappeared, and the spectrum consisted of two symmetric ferric peaks again.

It appears that with pressure the thiocyanate isomerizes to the isothiocyanate. This is a continuous process, since the isomer shift and quadrupole splitting of the ferrous peaks continuously increase with pressure (Figs. 2 and 3). The peak widths were essentially independent of pressure, so that we apparently had primarily one species at any one pressure. That is to say that, at any given pressure, each ferrous ion has essentially the same distribution of thiocyanate and isothiocyanate ligands. The ferric ion spectrum became more symmetrical with increasing pressure, so that the ferric complexes were also isomerizing. However, we could get no quantitative measure of the amount, nor could we establish the degree to which isomerization preceded or followed reduction.

The early portion of the conversion data for the thiocyanate (*open circles*) was fit with an equation of the usual form, but it is doubtful whether the constants *A* and *B* have physical significance, since the distribution of ligands varied with pressure.

If the starting material was heated to 110°C at 5 kb, the original asymmetric spectrum became more symmetric. As this heated material reduced under increasing pressure, two pairs of ferrous peaks appeared: one with an isomer shift of about 0.9 mm/sec and a quadrupole splitting of 1.1–1.2 mm/sec and one at

TABLE 3. Constants *A* and *B* in equation $K = AP^B$.

Compound	<i>A</i>	<i>B</i>
Fe(NCS) ₂	0.136	0.528
K ₂ Fe(NCS) ₄	0.0244	0.692
K ₂ Fe(SCN) ₄	0.75	0.298