

with increasing temperature. This is very reasonable as it takes thermal energy to cross the barrier between the potential wells. Hemin and hematin exhibited exothermic behavior. It would seem that thermal deformation of the potential wells must be the dominating effect for these systems.

High pressure studies have also been made on higher oxidation states of iron (9). SrFeO_3 contains Fe(IV). With pressure, this reduces to Fe(III). At 150 kbar, one observes about 65% Fe(III). The linear relationship between $\ln K$ and $\ln P$ is not obeyed. In BaFeO_4 iron is in the form Fe(VI). This apparently reduces to Fe(IV), with some production of Fe(III). The Fe(VI) is about 90% reduced at 150 kbar although impurities in the sample complicate the interpretation. It is evident that the ligand to metal electron transfer process is a very general one.

The Spin State of Iron

As was discussed in the Introduction, in a normal ionic compound or complex the 3d electrons on iron assume a configuration of maximum multiplicity. For the ferrous ion, when the ligand field parameter Δ approaches a value somewhat less than 2 eV, the balance between kinetic and potential energy begins to favor the low-spin arrangement. Since the crystal field tends to increase with pressure, one might expect that systems with a ligand field not too far below the critical value would undergo a high- to low-spin transition with increasing pressure. This transition, indeed, has been observed (10), but it is not the main point of the present discussion.

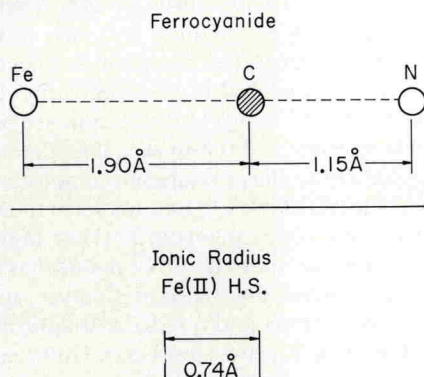
The ferrocyanides, ferricyanides, and substituted cyanides constitute perhaps the most interesting, and certainly the most widely studied, group of low-spin iron compounds. In these materials, the iron is surrounded in basically octahedral symmetry by six cyanide ions. (In the substituted cyanides, one of the CN^- is replaced by a different group and there may be a strong distortion from octahedral symmetry.) The iron is coordinated to the carbon end of the cyanide ion. The high-electron density at the iron nucleus (low isomer shift) and the small value for the interelectronic repulsion parameter both indicate that the 3d orbitals are strongly delocalized. The delocalization can be understood as follows. The cyanide ions have empty π^* orbitals. These can bond to the (filled) $t_{2g}(\pi)$ orbitals of the metal atom by *back donation* of metal electrons to the cyanide orbitals. Clearly, the degree of this back donation depends on the difference in energy between the π^* and t_{2g} orbitals. It is large when this energy difference is small and decreases as the energy

difference increases. This is an important point for our later discussion.

In this laboratory, we have observed the Mössbauer spectrum of five ferrocyanides— $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{Na}_4\text{Fe}(\text{CN})_6$, $\text{Zn}_2\text{Fe}(\text{CN})_6$, $\text{Ni}_2\text{Fe}(\text{CN})_6$, and $\text{Cu}_2\text{Fe}(\text{CN})_6$ (11)—to pressures of 200 kbar and temperatures of 150°C. At high pressure and high temperature an unexpected phenomenon occurred. A pair of peaks appeared in the spectrum with an isomer shift in the range 1.0–1.2 mm/sec and a quadrupole splitting ~ 2.0 mm/sec. These increased in intensity as either the pressure or temperature was increased. The possible explanations seem to be that one is producing either low-spin Fe(I) or high-spin Fe(II). It is known that the CN^- ligand has some tendency to stabilize low oxidation states, and the observed isomer shifts and quadrupole splitting are in a possible range for low-spin Fe(I). However, it is difficult to see how there would be energy available to transfer an electron to the e_g levels, some 4 eV above the filled t_{2g} levels. While this explanation cannot be completely discounted, there is a strong body of evidence that points towards the formation of high-spin Fe(II). The isomer shifts and quadrupole splitting lie within, but at the lower edge, of the usual range for high spin Fe(II). The conversion was reversible, but with considerable hysteresis. We were able to quench a sample of the copper salt which retained 18% conversion at one atmosphere according to its Mössbauer spectrum. A very sensitive Faraday balance indicated that this material had a magnetic susceptibility 1.75 times that of the starting material. This would indicate a conversion to high spin of 15–21% depending on whether one uses a *spin only* basis or ratios between susceptibilities of known low- and high-spin ferrous compounds. The infrared spectrum also revealed consistent information. In ordinary ferrocyanide the $\text{C}\equiv\text{N}$ stretching frequency is at 2180 cm^{-1} , a relatively low value compared with that for the free cyanide ion. The Fe–C stretching frequency is at 494 cm^{-1} . On the quenched sample there was a definite shoulder at 2260 cm^{-1} , much nearer the free cyanide value, and a peak at 467 cm^{-1} . Both of these observations are consistent with reduced metal to carbon bonding, which one would expect for high-spin Fe(II). (See also the discussion of $\text{Fe}[\text{Fe}(\text{CN})_5\text{NO}]$ below.) A weak peak appeared at $11,800\text{ cm}^{-1}$. This could be the crystal field peak of high-spin Fe(II). The uv spectrum was very poor, but it seemed that the transitions measuring the low-spin crystal field were shifted to lower energy.

A low- to high-spin transition with increasing pressure seems at first paradoxical in that for free

ions the low-spin ion would have the smaller volume. However, one must keep in mind that it is the volume of the system as a whole that must be considered. In ferrocyanides the bond distances are as shown below.



If one can speak of the *radius* of carbon in these circumstances, it must surely be less than 1.15 Å. The radius of high-spin Fe(II) is 0.74 Å. Thus, we can see that the delocalization of the iron orbitals results in a relatively large Fe-C distance, and a more compact high-spin arrangement is conceivable.

Let us first characterize the transition and then discuss the possible cause. Figure 5 shows the fraction of high spin versus pressure. The copper salt shows a large conversion at 110°C: There was measurable conversion even at 23°C. The nickel salt shows substantially less conversion at 110°C. The zinc salt showed only small conversion at 110°C, but considerably more at 147°C. The potassium and sodium salts showed only traces of conversion even

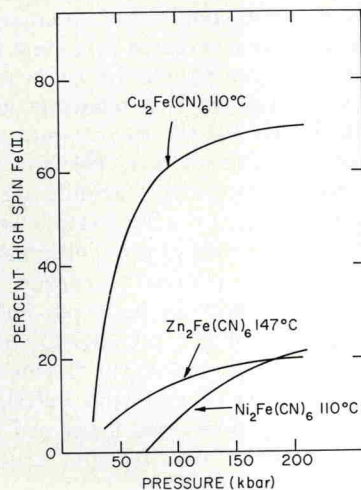


FIG. 5. Percent high-spin Fe(II) versus pressure—ferrocyanides.

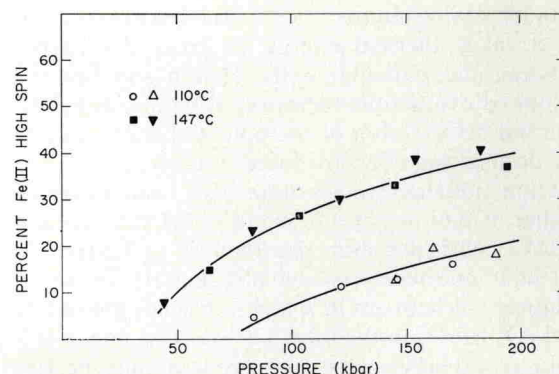


FIG. 6. Percent high-spin Fe(II) versus pressure—100 and 147°C—Ni₂Fe(CN)₆.

at 150°C and high pressure. Thus, the cation is important. Figure 6 for Ni₂Fe(CN)₆, shows that the low- to high-spin conversion increases measurably with increasing temperature.

A qualitative explanation of the phenomenon is possible. The observations on the reduction of iron with pressure indicate that the 3d orbitals lower in energy vis-à-vis the ligand orbitals as the pressure increases, so that iron increases its affinity for electrons. This change in energy level increases the energy difference between *t*_{2g} metal levels and the π^* ligand orbitals, and thus reduces the degree of back donation, which weakens the metal to CN⁻ bond.

If the back donation does decrease with increasing pressure, it should be reflected in the relative change in isomer shift with pressure for the low-spin ion. As Fig. 7 reveals, this is indeed so. The potassium and sodium salts, which undergo minimum conversion, show the usual decrease in isomer shift (increase in electron density at the nucleus) due to

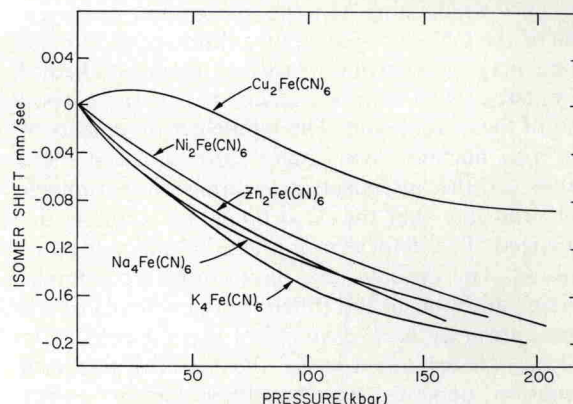


FIG. 7. Isomer shift—(relative to 1 atm) versus pressure—ferrocyanides.