

OXIDATION STATE OF FERRIC SALTS AT HIGH PRESSURES

By R. G. GARDINER,\* S. D. HAMANN,\* and M. LINTON\*

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Drickamer and his collaborators<sup>1-12</sup> have recently examined the Mössbauer spectra of a large number of solid compounds of iron at pressures up to 200 kbar (1 kbar =  $10^8$  N m<sup>-2</sup>  $\equiv$  986.92 atm). From the observed isomer shifts they have inferred that quite a small amount of compression causes the partial and reversible reduction of most ferric salts to ferrous ones. For example, ferric chloride<sup>4</sup> appears to convert into ferrous chloride to the extent of about 50% at 10 kbar and potassium ferricyanide<sup>3</sup> reduces to potassium ferrocyanide to the extent of 25% at the same pressure. Figure 1 summarizes the results for K<sub>3</sub>Fe<sup>III</sup>(CN)<sub>6</sub>. Drickamer *et al.*<sup>9,10</sup>

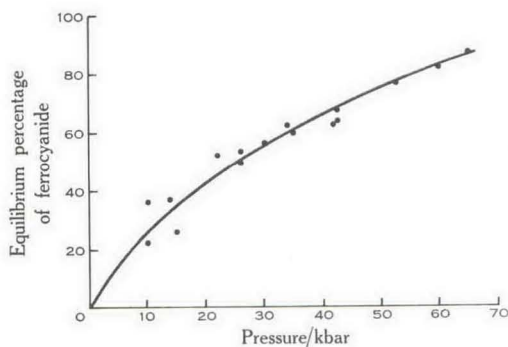


Fig. 1.—Mössbauer evidence of the reduction of potassium ferricyanide to potassium ferrocyanide (from Champion and Drickamer<sup>3</sup>).

consider that the conversion occurs through the transference of an electron from a ligand group to the metal atom. The effect is remarkable; it is unique in high-pressure chemistry and, if it is real, it must play an important role in the chemistry of the earth's interior.

\* Division of Applied Chemistry, CSIRO, P.O. Box 4331, Melbourne, Vic. 3001.

<sup>1</sup> Vaughan, R. W., and Drickamer, H. G., *J. chem. Phys.*, 1967, **47**, 468.

<sup>2</sup> Champion, A. R., Vaughan, R. W., and Drickamer, H. G., *J. chem. Phys.*, 1967, **47**, 2583.

<sup>3</sup> Champion, A. R., and Drickamer, H. G., *J. chem. Phys.*, 1967, **47**, 2591.

<sup>4</sup> Lewis, G. K., and Drickamer, H. G., *Proc. natn. Acad. Sci.*, 1968, **61**, 414.

<sup>5</sup> Fung, S. C., Lewis, G. K., and Drickamer, H. G., *Proc. natn. Acad. Sci.*, 1968, **61**, 812.

<sup>6</sup> Lewis, G. K., and Drickamer, H. G., *J. chem. Phys.*, 1968, **49**, 3782.

<sup>7</sup> Lewis, G. K., and Drickamer, H. G., *J. chem. Phys.*, 1968, **49**, 3785.

<sup>8</sup> Holzapfel, W., and Drickamer, H. G., *J. chem. Phys.*, 1969, **50**, 1480.

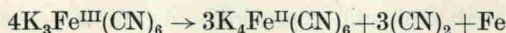
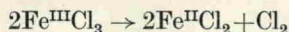
<sup>9</sup> Drickamer, H. G., Lewis, G. K., and Fung, S. C., *Science*, 1969, **163**, 885.

<sup>10</sup> Drickamer, H. G., Vaughan, R. W., and Champion, A. R., *Acc. chem. Res.*, 1969, **2**(2), 40.

<sup>11</sup> Fung, S. C., and Drickamer, H. G., *J. chem. Phys.*, 1969, **51**, 4353.

<sup>12</sup> Drickamer, H. G., Fung, S. C., and Lewis, G. K., *Adv. high Press. Res.*, 1969, **3**, 1.

However, it is a surprising effect for the following reasons. (i) There are already very large cohesive forces within ionic crystals at atmospheric pressure (their "internal pressures" are many kilobars) and it is strange that a superimposed hydrostatic pressure of only a few tens of kilobars should produce an entirely new and reversible chemical effect. (ii) Where it is possible to estimate the volume change that would accompany the reduction it turns out to be positive at normal pressures and it follows from Le Chatelier's principle that reduction should be suppressed, not favoured, by an increase of hydrostatic pressure. For instance, the densities of the condensed components show that the reactions



are accompanied by volume increases of 8.8 and 7.7 cm<sup>3</sup> per mole of Fe salt, respectively, and the increases would probably be slightly greater if free radicals rather than molecules were formed from the ligands. On the other hand, Drickamer's results imply that the reductions occur with volume decreases of several cm<sup>3</sup> per mole. (iii) The investigators have remarked that the reduction is sometimes only sluggishly reversible when the pressure is released<sup>11</sup> and that it nearly always shows "hysteresis", in the sense that the ferrous form does not completely revert to the ferric.<sup>2,4,6,9,12</sup> Neither feature would be expected of a simple electron transfer reaction. (iv) It is a little surprising that the reduction occurs only partially, instead of completely by the kind of sharp transition that is characteristic of valence and bonding changes in solids.

For these reasons we have sought independent evidence of reduction by examining the infrared spectra of some ferric salts at pressures up to 50 kbar.

The measurements were made in a high-pressure diamond optical cell, fitted into a 6 × microsampling unit in a Perkin-Elmer 521 spectrometer. The cell<sup>13</sup> and its mode of operation<sup>13-15</sup> have been fully described elsewhere. In the present experiments we used it without a gasketing device, simply placing the powdered salt between the diamond anvils and compressing it axially. Unfortunately, the infrared absorption of the diamonds and the unavoidable deficiencies of the optical system restricted use of the apparatus to the ranges 300-1900 cm<sup>-1</sup> and 2300-4000 cm<sup>-1</sup> and we were compelled to work with salts which absorb in those ranges and whose spectra there are sufficiently different in the ferric and ferrous forms. We were unable, for that reason, to obtain evidence of the behaviour of the ferric halides.

We selected potassium ferricyanide for detailed study because Drickamer<sup>3,11</sup> has found that it readily reduces to the ferrocyanide (Fig. 1) and because there are

<sup>13</sup> Weir, C. E., Lippincott, E. R., van Valkenburg, A., and Bunting, E. N., *J. Res. natn. Bur. Stand. (A)*, 1959, **63**, 55; Lippincott, E. R., Weir, C. E., van Valkenburg, A., and Bunting, E. N., *Spectrochim. Acta*, 1960, **16**, 58; Lippincott, E. R., Welsh, F. E., and Weir, C. E., *Analyt. Chem.*, 1961, **33**, 137; Whatley, L. S., Lippincott, E. R., van Valkenburg, A., and Weir, C. E., *Science*, 1964, **144**, 968; Whatley, L. S., and van Valkenburg, A., *Adv. high Press. Res.*, 1966, **1**, 327.

<sup>14</sup> Bradbury, M. G., Hamann, S. D., and Linton, M., *Aust. J. Chem.*, 1970, **23**, 511.

<sup>15</sup> Brasch, J. W., Melverger, A. J., Lippincott, E. R., and Hamann, S. D., *Appl. Spectrosc.*, 1970, **24**, 184.

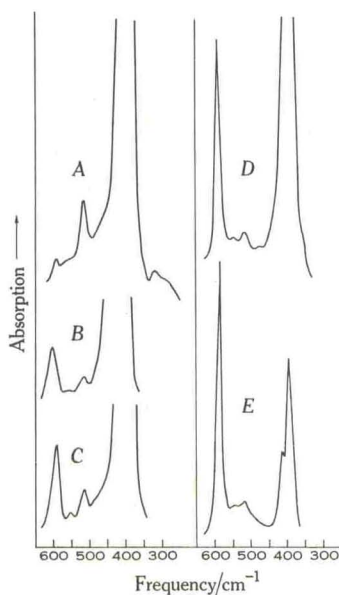


very marked differences in the spectra of the  $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$  and  $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$  ions in the region  $300\text{--}650\text{ cm}^{-1}$ .  $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6$  has a strong band  $\nu_8$  at  $388\text{ cm}^{-1}$  and a weak band  $\nu_7$  at  $508\text{ cm}^{-1}$ , whereas the corresponding bands in  $\text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6$  occur at  $416\text{ cm}^{-1}$  (medium) and  $584\text{ cm}^{-1}$  (strong). Nagakawa and Shimanouchi<sup>16</sup> suggested that  $\nu_7$  is primarily an Fe–C stretching vibration and  $\nu_8$  an Fe–C–N bending vibration, but Jones<sup>17</sup> later concluded that these assignments should be reversed. For our purpose the assignments are not important since we have merely used the bands as indicators of the amount of each salt present, by comparing the spectrum of compressed  $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6$  with the spectra of synthetic mixtures of the two salts.

The experiments were performed on a variety of commercial and purified samples of  $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6$ . The results varied slightly from one experiment to another for a particular sample and varied rather more for different samples, but in no case did we find any reversible transformation of the kind indicated in Figure 1. Instead, a small fraction of the salt underwent an *irreversible* conversion into ferrocyanide when it was first compressed, and subsequent cycles of compression and decompression produced further progressive transformation to ferrocyanide.\*

Fig. 2.—Infrared spectra of potassium ferricyanide in a diamond cell.

- A, Initial spectrum at atmospheric pressure;  
 B, spectrum measured at 50 kbar after the first compression;  
 C, spectrum after the release of pressure from B;  
 D, spectrum at atmospheric pressure after four compression cycles;  
 E, spectrum at atmospheric pressure after eight compression cycles.



This behaviour is illustrated by the series of spectra in Figure 2, where *A* is the initial spectrum of  $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6$  in the diamond cell at atmospheric pressure; it contains a very weak band at  $584\text{ cm}^{-1}$  caused by a trace ( $<0.2\%$ ) of ferrocyanide, which we could never completely remove from the starting material. Spectrum *B*

\* We are not sure that  $\text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6$  was the only product. Other ferrocyanides such as Prussian blue,  $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$ , may have been formed and would probably have had very similar infrared spectra. The amount of material was too small to be analysed chemically, but it sometimes had a bluish colour.

<sup>16</sup> Nagakawa, I., and Shimanouchi, T., *Spectrochim. Acta*, 1962, **18**, 101.

<sup>17</sup> Jones, L. H., *Inorg. Chem.*, 1963, **2**, 777.

shows that, on compression to 50 kbar, this band was intensified, broadened, and shifted to  $596\text{ cm}^{-1}$ , and the strong ferricyanide band at  $388\text{ cm}^{-1}$  was broadened and shifted to  $395\text{ cm}^{-1}$ . The relative intensities of the two bands showed that about 2% of the ferricyanide had transformed to ferrocyanide. When the pressure was released (spectrum *C*) the  $596\text{ cm}^{-1}$  band returned to  $584\text{ cm}^{-1}$  but its integrated intensity remained much the same. Clearly an irreversible conversion occurred between *A* and *B*, and there is no sign in the spectra of the 75% reversible conversion expected from Figure 1. Spectrum *D* shows that after four cycles of compression and decompression the amount of irreversible transformation reached about 15%, and *E* shows that it reached about 50% after eight cycles. By that time a considerable amount of extrusion had occurred and the whole spectrum was much weaker than *A*.

Our results confirm some observations made by Klyuev and Vorob'ev,<sup>18</sup> using an entirely different kind of high-pressure optical cell,<sup>19</sup> rather like Drickamer's Mössbauer cell.<sup>20</sup> They examined several bands of  $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6$  in the regions of  $2000\text{ cm}^{-1}$  and  $4000\text{ cm}^{-1}$  at pressures up to 23 kbar and concluded that compression causes an irreversible transformation to ferrocyanide.

The type of progressive conversion which we have found is characteristic of reactions that are caused by a combination of shearing stress with compression. We have observed it before in some solid-phase polymerization reactions.<sup>14</sup> Each time the salt is compressed it is subjected to radial shearing forces and is partly extruded, so that the cumulative effect is similar to that produced by Bridgman's method<sup>21</sup> of combining deliberate torsional shearing with uniaxial compression. Significantly, Drickamer himself has reported<sup>22</sup> that  $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6$  transforms almost completely to  $\text{K}_4\text{Fe}^{\text{II}}(\text{CN})_6$  when it is deliberately deformed in a Bridgman shearing device.\*

Unfortunately, it is very difficult to compress a polycrystalline solid without generating shearing stresses (in Drickamer's apparatus they may have been quite large). For that reason we have examined the ultraviolet spectrum of  $\text{K}_3\text{Fe}^{\text{III}}(\text{CN})_6$  solutions in water, where the ions are under true hydrostatic pressures. A pressure of 2 kbar shifted the  $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$  band reversibly from  $23810\text{ cm}^{-1}$  to  $23650\text{ cm}^{-1}$  but produced no measurable change (i.e.  $> \frac{1}{2}\%$ ) in the optical density. We should have expected a decrease of several per cent in optical density if the ions had been reduced to the extent shown in Figure 1.

As well as potassium ferricyanide, we have examined the following salts in the diamond cell at pressures up to 50 kbar: basic ferric acetate, ferric citrate, ferric

\* The restrictions of Le Chatelier's principle, discussed in the second paragraph of this paper, apply only under equilibrium and hydrostatic conditions, whereas shearing conditions are non-equilibrium and non-hydrostatic in nature. It is known, for instance, that high pressure shearing can cause explosions<sup>21, 23-25</sup> which involve large and obvious increases of volume.

<sup>18</sup> Klyuev, Yu. A., and Vorob'ev, A. M., *Proc. Acad. Sci. USSR (Phys. Chem. Sec.)*, 1964, **158**, 975.

<sup>19</sup> Klyuev, Yu. A., *Instrum. exp. Tech. (USSR)*, 1964, 174.

<sup>20</sup> Debrunner, P., Vaughan, R. W., Champion, A. R., Cohen, J., Moyzis, J. A., and Drickamer, H. G., *Rev. scient. Instrum.*, 1964, **35**, 29.

<sup>21</sup> Bridgman, P. W., *Phys. Rev.*, 1935, **48**, 825.

<sup>22</sup> Larsen, H. A., and Drickamer, H. G., *J. phys. Chem.*, 1957, **61**, 1249.

<sup>23</sup> Bridgman, P. W., *Proc. Am. Acad. Arts Sci.*, 1937, **71**, 422.

<sup>24</sup> Malmrud, S., and Claesson, S., *Ark. Kemi*, 1966, **25**, 201.

<sup>25</sup> Hamann, S. D., *Aust. J. Chem.*, 1967, **20**, 605.



oxalate, ferric tartrate, ferric ammonium chloride, ferric ammonium citrate, and ferric ammonium sulphate. In no instance was there any evidence of reversible conversion to ferrous salts. Only ferric oxalate showed a marked reversible change in its spectrum, and it was of the kind characteristic of polymorphic transitions:<sup>15</sup> the high pressure form was not ferrous oxalate.

To summarize, we have failed to find any infrared evidence that ferric salts transform reversibly to ferrous ones at the pressures where Drickamer's Mössbauer measurements indicate that they do. At this stage it is not profitable to speculate on the reasons for the discrepancy, but we suggest that until the Mössbauer measurements can be repeated under nearly hydrostatic conditions it would be wise to treat the results with caution.