

OXIDATION STATE OF FERRIC SALTS AT HIGH PRESSURES

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[Manuscript received July 10, 1970]

Drickamer and his collaborators¹⁻¹² 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⁻² \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 chloride⁴ appears to convert into ferrous chloride to the extent of about 50% at 10 kbar and potassium ferricyanide³ reduces to potassium ferrocyanide to the extent of 25% at the same pressure. Figure 1 summarizes the results for K₃Fe^{III}(CN)₆. Drickamer *et al.*^{9,10}

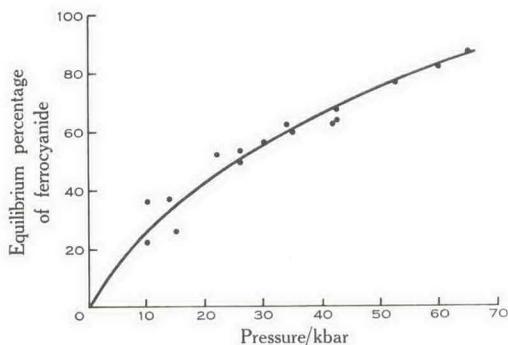


Fig. 1.—Mössbauer evidence of the reduction of potassium ferricyanide to potassium ferrocyanide (from Champion and Drickamer³).

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.

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

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

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

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

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

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

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

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

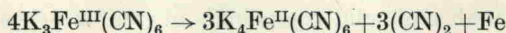
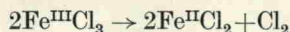
⁹ Drickamer, H. G., Lewis, G. K., and Fung, S. C., *Science*, 1969, **163**, 885.

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

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

¹² 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 cm³ 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 cm³ per mole. (iii) The investigators have remarked that the reduction is sometimes only sluggishly reversible when the pressure is released¹¹ and that it nearly always shows "hysteresis", in the sense that the ferrous form does not completely revert to the ferric.^{2,4,6,9,12} 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 cell¹³ and its mode of operation¹³⁻¹⁵ 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⁻¹ and 2300-4000 cm⁻¹ 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^{3,11} has found that it readily reduces to the ferrocyanide (Fig. 1) and because there are

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

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