

presence of the other, and to estimate the relative amounts of the two states from computer fit areas. Although the difference in low spin states is less spectacular, the calculation is still possible. Perhaps the most remarkable of the high pressure Mössbauer observations is that ferric iron reduces to ferrous iron with increasing pressure in a wide variety of compounds, and that this is essentially a reversible process. This has been discussed in a series of articles including Champion *et al.* (1967), Champion and Drickamer (1967a, b), Lewis and Drickamer (1967a), and Fung (1968).

As an example, a series of spectra for FeCl_3 are shown in Figs 22(a, b). The process reverses upon release of pressure, but with considerable hysteresis. On removing the pellet and powdering the sample one almost always recovers the atmospheric spectrum. A greater or lesser degree of conversion has been observed in FeCl_3 , FeBr_3 , KFeCl_4 , FePO_4 , $\text{Fe}_2(\text{SO}_4)_3$, $\text{Fe}(\text{NCS})_3$, $\text{Fe}(\text{NH}_3)_6\text{Cl}_3$, $\text{K}_3\text{Fe}(\text{CN})_6$, ferric citrate, basic ferric acetate, ferric acetyl acetonate, ferric oxalate, various hydrates, hemin and hematin.

The form of the pressure dependence is essentially always the same, as is illustrated in Figs 23 and 24. If one defines an equilibrium constant $K = C_{\text{II}}/C_{\text{III}}$, then

$$K = AP^B \quad (28)$$

where A and B are independent of pressure. Typical values for these constants are shown in Table IV. It has been shown that one is observing true equilibrium and not the results of slow kinetics by the fact that successive spectra run at the same pressure are substantially identical.

The reaction is almost always endothermic, that is the conversion increases with increasing temperature, although in the case of hemin the conversion actually decreases with increasing temperature. The heat of reaction generally is in the range 0.1–0.3 eV, and usually increases with increasing temperature. For the most ionic systems the heat of reaction does not depend significantly on pressure, but in more covalent materials it may increase or decrease sharply with increasing pressure.

One is faced with two problems in discussing these results: why does the electron from ligand to metal take place, and why does the reaction have the observed pressure dependence, that is why does one not obtain discontinuous ferric to ferrous conversion at some pressure.

As discussed in the introduction, it is possible to excite an electron optically from the non-bonding ligand levels to the lowest antibonding metal levels ($t_{2u} \rightarrow t_{2g}$ in octahedral symmetry). This optical charge

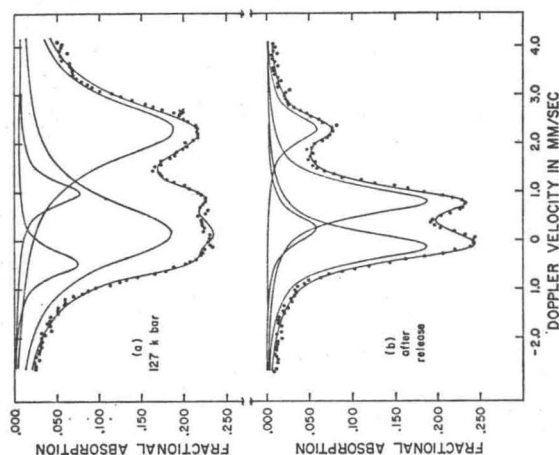


Fig. 22b. Mössbauer spectra for FeCl_3 continued.

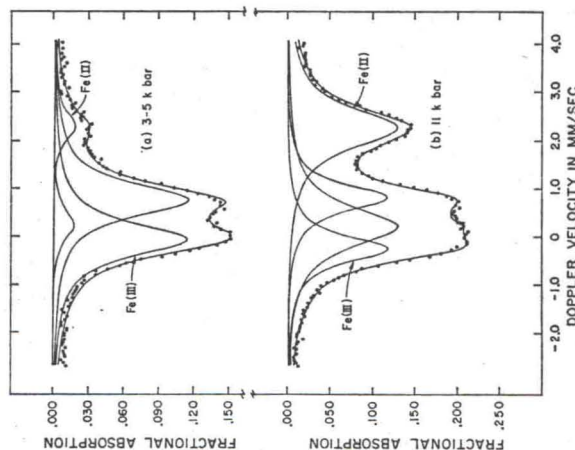


Fig. 22a. Mössbauer spectra for FeCl_3 .