

volume and a distortion. This affects the neighbouring complexes, distorting the potential wells in such a way as to make electron transfer less favourable. With increasing pressure the excited state is lowered further and one obtains more conversion, but with further increase in local strain. The sluggishness and hysteresis with which the process reverses on release of pressure can be associated with the stored up strain.

The situation can be described thermodynamically:

$$K = \exp(-\Delta G/RT) \quad (29)$$

$$\frac{\partial \ln K}{\partial \ln P} = -\frac{P\Delta\bar{V}}{RT} = \frac{P(\bar{V}^{\text{III}} - \bar{V}^{\text{II}})}{RT} \quad (30)$$

where \bar{V}^{III} and \bar{V}^{II} refer to the partial molar volumes of the ferric and ferrous sites plus their associated ligands.

From our empirical observation

$$\frac{\partial \ln K}{\partial \ln P} = B \quad (31)$$

where B is a constant. One can rearrange eqn (29), remembering that $K = C_{\text{II}}/1 - C_{\text{II}}$. Then

$$\frac{\partial \ln C_{\text{II}}}{\partial \ln P} = \frac{P(\bar{V}^{\text{III}} - \bar{V}^{\text{II}})}{RT} (C_{\text{III}}). \quad (32)$$

Thus, the fractional increase in conversion with fractional increase in pressure is proportional to C_{III} , the number of sites available for conversion. The proportionality coefficient is the work necessary to form a ferrous site from a ferric site, measured in thermal units (that is in units of RT). It is entirely reasonable that in the first order the dependence would be first order in these variables, and that to the first approximation the coefficient is a constant. Experimentally, it appears that higher order terms are negligible.

F. HIGH PRESSURE MÖSSBAUER STUDIES ON GLASS

An interesting application of high pressure Mössbauer resonance is the investigation of the structure of glass. Lewis and Drickamer (1968) and Kurkjian and Sigety (1964) have made extensive studies, correlating the atmospheric Mössbauer spectrum of ferric ions with the site symmetry. Tischer and Drickamer (1962) have studied the effect of pressure on the optical spectra of a number of transition metal ions

in various glasses. The work discussed here involves Mössbauer studies of Fe^{III} and Fe^{II} ions in a phosphate and in a silicate glass.

The phosphate glass consists of chains of PO_4^- tetrahedra with little crosslinking, in contrast to the silicate glass discussed below. Both the ferric and the ferrous ions are in octahedral sites in the phosphate glass. High pressure Mössbauer resonance studies have also been made on FePO_4 and $\text{Fe}_3(\text{PO}_4)_2$ in the crystalline state (Champion *et al.*, 1967a). The Fe^{III} ion in the glassy medium behaved in much the same way as it did in the crystal. This is illustrated in the change in isomer shift and quadrupole splitting for the Fe^{III} ion in Figs 26 and 27.

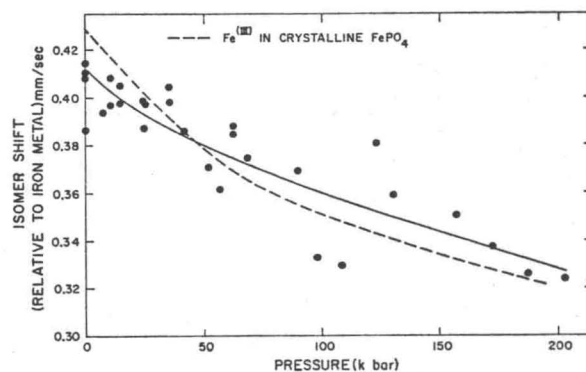


FIG. 26. Isomer shift versus pressure— Fe^{III} in phosphate glass.

The ferric ion reduced to the ferrous state with pressure in the glass as it did in the crystal but with different coefficients A and B . These are listed in Table IV in the previous section. The behaviour of the Fe^{II} ion in the phosphate glass was also quite similar to that in the crystal.

The silicate glass, in addition to chains and rings, includes three dimensional networks. Kurkjian and Sigety (1964) have shown that the ferric ion is in a tetrahedral site in silicate glass, while Tischer and Drickamer (1962) indicate that the ferrous ion is in a loose octahedral site. Weyl (1951) shows that the ferric ion is both a network former and a network modifier in silicate glass, that is it can replace a silicon or be in an interstice. Ferrous ion is always a network modifier.

The isomer shift for Fe^{III} ion is shown as a function of pressure in Fig. 28. One observes an increase with increasing pressure in the low