where B is the bulk modulus, one obtains the relationship:

$$\ln K = -\frac{\Delta G_1}{kT}(1 + y)^{1/16}\left[1 + \frac{\Delta G_5}{\Delta G_1}(1 + y)^{1/4} + \frac{\Delta G_9}{\Delta G_1}(1 + y)^{1/2}\right] \quad 8.$$

where $y = nP/B$ and the ΔG values correspond to the three types of interaction mentioned above. Reasonable values of ΔG indeed predict a pressure-conversion dependence qualitatively similar to experiment. The fact that the conversion spreads over a large range of pressure depends on the relative importance of the three terms in various pressure regions. The fit to the data, however, requires rather close cancellation between ΔG_1 and ΔG_5 which seems fortuitous for so many compounds over a large pressure range.

For a really satisfactory discussion of the data, it is necessary to assume interacting centers. One expands Γ:

$$\Gamma(P_1T) = \Gamma_0(T) + P\Gamma_1(T) + P^2\Gamma_2(T) \quad 9.$$

The results of this analysis are most striking in establishing reasonable pressure and temperature dependence for the equilibrium constant.

$$\frac{d\ln K}{d\ln P} = \left[\frac{1}{1 - \frac{\Gamma_0}{kT}\left[\frac{2K}{(1 + K)^2}\right]}\right]\left(\frac{d\ln K}{d\ln P}\right)_{\Gamma_0 = 0} \quad 10.$$

for $K = 1$ this reduces to

$$\frac{d\ln K}{d\ln P} = \frac{1}{\left(1 - \frac{\Gamma_0}{2kT}\right)}\left(\frac{d\ln K}{d\ln P}\right)_{\Gamma_0 = 0} \quad 11.$$

Relatively small values of Γ_0 affect the slope significantly, e.g. for a repulsive interaction with $\Gamma_0 = -0.05$ eV the slope is cut in half. The introduction of Γ makes it possible to fit a wide variety of data rather easily. For the temperature dependence one obtains

$$\frac{d\ln K}{d(1/T)} = -\frac{1}{k}\left[\frac{\Delta H + \left(\frac{1 - K}{1 + K}\right)\left(\Gamma - T\frac{d\Gamma}{dT}\right)}{1 - \frac{2\Gamma}{kT}\frac{K}{(1 + K)^2}}\right] = -\frac{\Delta H_{\mathrm{eff}}}{k} \quad 12.$$

So that if the interaction is repulsive (Γ-negative) the effective heat of reaction is reduced. For attractive interaction the possibility exists that the denominator might go to zero, which corresponds to a discontinuity in conversion at some temperature. This phenomenon has been observed by König & Madeja (71) for the spin transition in certain ferrous phenanthrolines.

This analysis lends itself to rather extensive graphical presentation which appears in Slichter and Drickamer's paper. It is possible to establish the effects of both attractive interaction, which enhances conversion, and repulsive interaction, which inhibits it. The possibilities of hysteresis and of a discontinuity in the degree of conversion at some temperature and pressure are also illustrated.

Summary

Pressure has profound effects on the electronic structure of solids. One of the most general and significant of these is the relative shift in energy of one type of orbital with respect to another. For a wide variety of materials there exist excited states which lie sufficiently near the ground state so that this relative shift can create a new ground at high pressure or greatly modify the ground state by configuration interaction. These new ground states may have very different properties which lead to new electronic and chemical phenomena. A study of this new chemistry and physics can also enhance our understanding of atmospheric pressure chemical and physical phenomena.

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