

Figure 1. The experimental proton $T_{1\rho}$ and T_1 results for cyclohexane at 270 K plotted as a function of hydrostatic pressure. ● $T_{1\rho}$ at $H_1 = 10.0$ G; ○ $T_{1\rho}$ at $H_1 = 2.0$ G; △ T_1 .

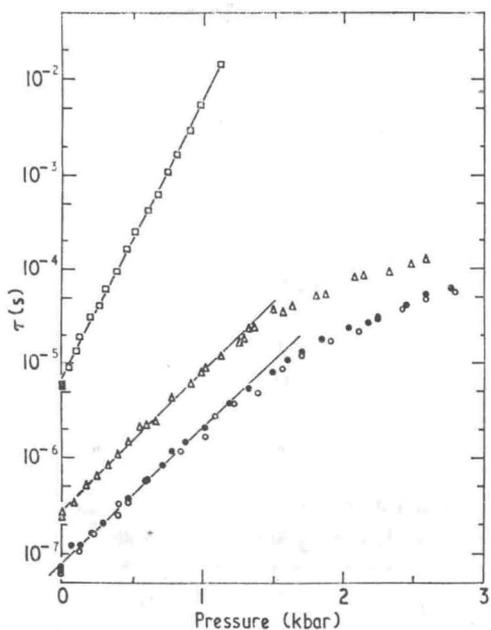


Figure 2. The translational correlation times τ for self diffusion plotted as a function of hydrostatic pressure. □ Hexamethylethane; △ Norbornylene; ○ cyclohexane ($H_1 = 2.0$ G); ● cyclohexane ($H_1 = 10.0$ G).

Measurements of the temperature dependence of $T_{1\rho}$ in these materials have previously been interpreted using a weak collision theory (Jones 1966) and correlation functions appropriate to a random walk model for self diffusion (Resing and Torrey 1963) with an average molecular jump time τ . Analysing our values of $T_{1\rho}$ in the same manner, we obtain τ as a function of pressure for each material, figure 2. In our analysis it is assumed that the strength of the intermolecular nuclear dipolar interaction is not pressure dependent. If the bulk compressibility is similar to that of comparable plastic crystals (Breitling *et al* 1971) the change in the strength of this interaction is unlikely to exceed 20% over the pressure range studied, whereas τ changes by two to three orders of magnitude. In the case of cyclohexane and norbornylene $T_{1\rho}$ passes through a minimum with increasing pressure. Since the depth of these minima is the same as the depth of minima obtained in temperature dependence studies at low pressure no significant change in this interaction had occurred. The values of τ obtained for cyclohexane from measurements at two different H_1 intensities are consistent (figure 2), thereby giving a useful check on our analysis.

A thermodynamic treatment of self diffusion (Shewmon 1963) provides an expression for the self diffusion coefficient

$$D = \gamma a_0^2 \nu \exp\left(\frac{-\Delta G^*}{RT}\right) \quad (1)$$

where γ is a geometric factor, ν is the lattice vibration frequency, ΔG^* is the free energy of activation and a_0 is the lattice parameter. When self diffusion proceeds by molecular jumps of uniform distance a the self diffusion coefficient is related to τ by

$$D = a^2/6\tau \quad (2)$$

Therefore

$$\tau = \frac{a^2}{6\gamma a_0^2 \nu} \exp\left(\frac{\Delta G^*}{RT}\right) \quad (3)$$

The activation volume is defined as $\Delta V^* = [\partial(\Delta G^*)/\partial P]_T$ so that, using equation 3, ΔV^* is given by

$$\Delta V^* = RT \left(\frac{\partial \ln \tau}{\partial P} + \frac{\partial \ln \nu}{\partial P} \right)_T \quad (4)$$

Only the term $[\partial(\ln \tau)/\partial P]_T$ in equation 4 is determined from our experiment. Unfortunately, for these plastic crystals, data enabling calculation of $[\partial \ln \nu / \partial P]_T$ are not available. We estimate, using data for similar plastic crystals (Breitling *et al* 1971), that this term is unlikely to exceed 10% of ΔV^* . The tabulated values of ΔV^* represent only the first term in equation 4.

At pressures below 1.4 kbar $\ln \tau$ shows a linear dependence on pressure from which ΔV^* in the table is calculated. It can be seen that the ratios $\Delta V^*/V_m$ are of the order of unity suggesting a vacancy mechanism for self diffusion in these solids. The ratio is lower than unity for the two compounds with low ΔS_m . It is very similar to those found for close packed metals where single vacancy mechanisms and inward relaxation of surrounding molecules into a vacancy are generally accepted. For hexamethylethane (bcc) the ratio of 1.2 is significantly greater than the values ($\lesssim 0.5$) found for bcc metals.

Our value of ΔV^* , 71 ml mol⁻¹, for cyclohexane is considerably greater than the value 13 ml mol⁻¹ previously reported (Anderson and Slichter 1966b). This earlier value was obtained by measurement of the spin-spin relaxation time T_2 on unpurified reagent