

## Pressure dependence of self diffusion in the plastic crystals hexamethylethane, norbornylene and cyclohexane

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**Abstract.** Translational self diffusion in three molecular crystals has been studied as a function of pressure using nuclear spin-lattice relaxation time measurements. Activation volumes are obtained which are consistent with a vacancy diffusion mechanism.

Molecular crystals exhibiting a plastic crystalline phase are generally composed of globular molecules which are undergoing rapid reorientational motion. A consequence of this is that the entropies of fusion are low ( $\Delta S_f \lesssim 20 \text{ eu}^\dagger$ ). It has been noted (eg Bladon *et al* 1971) for plastic crystals with relatively high entropies of fusion ( $\Delta S_f > 17 \text{ eu}$ ) that the activation enthalpy for self diffusion,  $\Delta H^*$ , is approximately twice the latent heat of sublimation,  $L_s$ . For these plastic crystals the activation enthalpies obtained by nuclear magnetic resonance (NMR) techniques are in good agreement with those obtained by radiotracer and creep measurements. Agreement between these techniques for materials with lower  $\Delta S_f$  is not so good (Bladon *et al* 1971) and discrepancies have been tentatively attributed to relaxation around vacancies. It has been suggested (Jost 1960, Hood and Sherwood 1966a) that since  $L_s$  is a measure of the lattice energy, the observation that  $\Delta H^* \simeq 2L_s$  implies a single vacancy mechanism for self diffusion. Plastic crystals with relatively low entropies of fusion ( $\Delta S_f < 17 \text{ eu}$ ) have revealed self diffusion activation enthalpies, as determined by NMR, which are in the range  $L_s < \Delta H^* \lesssim 2L_s$ . This is consistent with vacancy formation parameters obtained by Baughman and Turnbull (1971) from analysis of excess heat capacity in similar systems. These authors suggest considerable vacancy relaxation may be responsible for the low vacancy formation enthalpies in the low  $\Delta S_f$  materials. In the case of cyclohexane ( $\Delta S_f = 9.2 \text{ eu}$ ) radiotracer measurements of the isotope effect have suggested that many neighbouring atoms (about twelve) are cooperatively involved in the microscopic diffusion step (Chadwick and Sherwood 1972.)

The temperature dependence of the proton spin-lattice relaxation time in the rotating frame,  $T_{1\rho}$ , for hexamethylethane (Chezeau *et al* 1971), norbornylene (Folland *et al*, to be published) and cyclohexane (Roeder and Douglass 1970) has been measured under their equilibrium vapour pressures. The correlation times for translational self diffusion have been deduced for the plastic phase in each case. Self diffusion coefficients have also been determined by radiotracer studies in hexamethylethane (Lockhart and Sherwood, to be published) and cyclohexane (Hood and Sherwood 1966b). In the case of hexamethylethane ( $\Delta S_f = 20 \text{ eu}$ ) results obtained by the two methods are in good agreement. However, for cyclohexane ( $\Delta S_f = 9.2 \text{ eu}$ ) the activation enthalpy from radiotracer measurements ( $\Delta H^* = 68.2 \text{ kJ mol}^{-1}$ ) differs significantly from the NMR

$\dagger 1 \text{ eu} \equiv 1 \text{ J K}^{-1} \text{ mol}^{-1}$

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