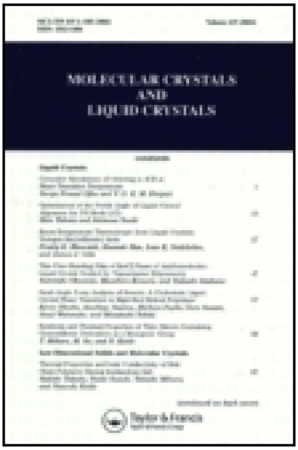

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Self Diffusion in Cyclohexane Single Crystals

G. M. Hood [a] [b] & J. N. Sherwood [a]

[a] Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow

[b] Pure Chemistry Division, National Research Council, Ottawa, Canada

Version of record first published: 21 Mar 2007.

To cite this article: G. M. Hood & J. N. Sherwood (1966): Self Diffusion in Cyclohexane Single Crystals, Molecular Crystals, 1:1, 97-112

To link to this article: http://dx.doi.org/10.1080/15421406608083263

Molecular Crystals. 1966. Vol. 1, p. 97–112

Printed in Great Britain

Self Diffusion in Cyclohexane Single Crystals

G. M. HOOD† and J. N. SHERWOOD
Department of Pure and Applied Chemistry,
University of Strathclyde, Glasgow

Received September 3, 1965

Abstract—Self diffusion has been studied in single crystals of cyclohexane in the plastic crystalline phase of this solid. In the temperature range $-70°$ C to $-30°$ C there appears to be one diffusion mechanism in operation which is best described by an equation

$$D = 3.9 \times 10^6 \exp - (16{,}300 \pm 300/RT) \text{ cm}^2 \text{ sec}^{-1}.$$

It is proposed that diffusion occurs by the random walk of relaxed vacancies in the lattice. The concentration of these defects is much higher at the melting point than in other types of solid. It is possible that this high defect concentration could account for the extreme plasticity of this solid.

Organic solids with molecules of almost spherical symmetry exist, in general, in two crystallographic modifications. The low temperature form has the normal physical characteristics of organic solids. At the crystallographic transition this normal solid is transformed into a face—or body—centred cubic modification which persists to the melting point. This high temperature form is usually waxy in appearance and behaves under stress like an extremely viscous liquid. These solids in this form, have come to be known as Plastic Crystals.[1]

The transition to the plastic phase is accompanied by a large entropy change, $\Delta S_t = 10–15$ e.u.; the plastic form subsequently melting with a low entropy of fusion $\Delta S_f < 5$ e.u. Consideration of this thermodynamic evidence and the physical nature of the solid, has led to the speculation that the molecules have a considerable orientational disorder in the solid state. On melting they will have little more to gain than translational mobility. Numerous investigations of molecular motions in these solids do indicate

---

† Present address: Pure Chemistry Division, National Research Council, Ottawa, Canada.

that there is a considerable degree of rotational molecular mobility above the crystallographic transition.[2]

Nuclear magnetic resonance experiments[3] with these crystals have confirmed this appearance of rotational freedom at the transition point. These experiments also indicate that, at temperatures approaching the melting point, a translational motion commences. This motion (self diffusion) is almost as rapid as in the liquid phase. Up to the present time no direct study of the diffusion process has been attempted to confirm this. The only studies of diffusion in an organic solid, anthracene,[4, 5] indicate that self diffusion in a normal organic crystal will be slow. Diffusion studies in other classes of solids have helped in the elucidation of the defect structure in solids. In order to determine whether the n.m.r. experiment does observe self diffusion and to obtain a better understanding of the crystalline disorder in the plastic phase we have attempted a radiotracer study of self diffusion in single crystals of a plastic solid, cyclohexane, for which n.m.r. data are available.[6]

Experimental

CRYSTAL GROWTH

The purification and growth of the single crystals used for the experiments are described elsewhere.[7]

The crystals, obtained in the form of cylinders 1 cm diam. × 5 cm long, contained less than 0.01 mole % of impurity as determined by freezing curves. Microscopic examination of thermally etched crystals showed them to be free of the grain boundary sub-structure which appears on rapid freezing of the liquid. This sub-structure results from the segregation of impurities along boundaries in the crystal.[8] We conclude that, during the slow growth of the single crystals, any remaining impurity is segregated to the surface and hence the crystal is always much purer than the melt from which it is grown. In the high temperature modification cyclohexane crystallizes in a face-centred cubic structure; one major axis of the crystal was always parallel to the cylindrical axis of the boule.

The crystals were optically transparent with no cracks or striations. They were soft and waxy and were easily shaped with a sharp blade.

RADIOACTIVE MATERIAL

0.1 mc of cyclohexane-1-C14, specific activity 0.1 mc/mmole, obtained from the Radiochemical Centre, Amersham, was diluted *in vacuo* with 1 ml of pure cyclohexane. This cyclohexane was used for all experiments and was stored under vacuum in the deposition apparatus.

PREPARATION OF THE DIFFUSION COUPLE

Because of the low melting point of cyclohexane (6.55° C) the handling of the crystals presented a considerable difficulty. This was overcome by performing all manipulations in a deep freeze unit converted to act as a cold box at $-30°$ C. The deposition of the radioactive material and subsequent handling was carried out using the specially designed holder depicted in Fig. 1.

The single crystal in the form of a cylinder 1 cm diam. × 1 cm long, was placed in the cooled cup (A). Liquid cyclohexane was poured around it, this froze immediately holding the crystal in place. A locking ring was secured around the crystal as an added precaution. The crystal in the cup was attached to the chuck of a microtome by the rod (B). The face of the crystal was aligned with the blade and several sections removed from the surface. This served two purposes: the preparation of a flat surface for the application of the deposit and, since the microtome chuck was designed so that B could be relocated in the exact same position after the diffusion experiment, also for the location of the zero plane for sectioning.

After preparation the cup was screwed into the brass flange, (C) so that the crystal face just touched the plate. The hole in the flange was slightly smaller than the crystal and defined the area of crystal surface upon which the radioactive material would be deposited. The screw thread was rendered vacuum tight by the use of P.T.F.E. tape. The unit was transferred to the vacuum apparatus and the temperature of the crystal reduced to −70° C by pouring liquid air on to the surrounding blanket of cellulose wadding (E). The crystal temperature was monitored by the thermistor (T) the relationship between crystal temperature and thermistor temperature having been determined previously. The chamber was evacuated.

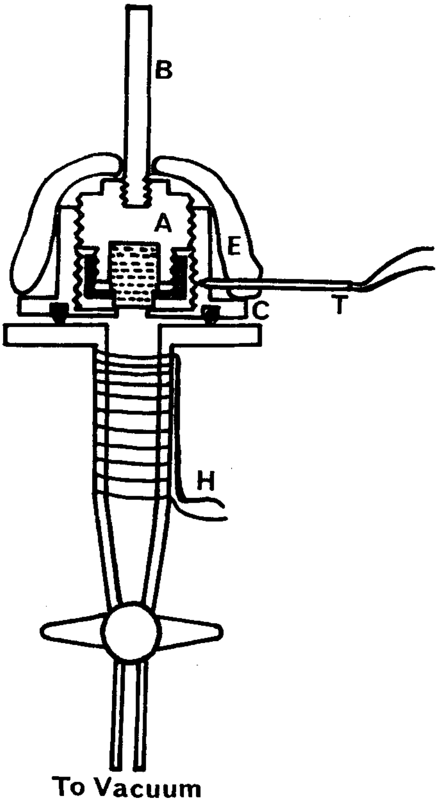

Figure 1. The deposition unit.

A measured volume of radioactive cyclohexane was transferred from a reservoir and allowed to condense on the crystal surface.

The heater (H) prevented condensation on the lower walls of the tube. It was found that the greater part of the vapour did deposit on the actual crystal surface. The average deposit was 1 mg of radioactive material which formed a layer 2 μ thick.

The holder was removed from the vacuum line. A thin piece of mica was placed across the hole in the flange to isolate the deposit and was held in place by a cork washer and screwed metal cap. This operation was performed as quickly as possible so that the crystal temperature would not rise to a point where rapid diffusion might occur. Experiment showed that during this operation the crystal temperature did not rise above $-65°$ C.

When sealed, the crystal holder was transferred to a low temperature thermostat bath. The crystal attained bath temperature in 2–3 min after immersion. The temperature was monitored by a thermistor attached to the crystal holder and was found to be constant to $\pm 0.05°$ C for the periods of the experiment. Experiments were carried out at temperatures in the range $-70°$ C to $-30°$ C for periods of 135 to 2090 min. Experiments at higher temperatures were not possible because of the high plasticity of the crystals.

DETERMINATION OF THE ACTIVITY PROFILE

The diffusion profile was determined by a sectioning technique using a microtome. This instrument is ideal for this purpose where these very soft crystals are involved. In these experiments a Beck Rotary Microtome was set up in the cold box and the movement calibrated, using a precision microscope and by cutting and weighing material. It proved possible to remove and collect a complete section of this waxy solid each time with no losses.

On completion of the diffusion period the crystal holder was removed from the thermostat. The crystal was relocated in the microtome chuck by the rod and 15 μ slices removed. Since it had been demonstrated that quantitative collection of the section was achieved, only occasional sections were weighed during the diffusion experiments. The purpose of this procedure was to eliminate errors due to evaporation.

After cutting, the sections were transferred to 15 ml sample vials and were diluted immediately with 10 ml of liquid scintillator solution [3 g diphenyl oxazole, 0.03 g 1,4-bis-2-(5-phenyloxazolyl) benzene in 1 l. scintillation grade toluene]. Following dark and temperature adaption the samples were counted in a modified Ecko N664B scintillation counter. The pulses were fed via a Nuclear Enterprises NE 5202 linear pulse amplifier and NE 5102 pulse height selector to a Dynatron 1009 e scaler. The small amounts of cyclohexane in each section (1–2 mg) had no quenching effect upon the scintillations. The overall counting efficiency of the system was 60% with a background of 0.2 counts/sec. Count rates, corrected for background were measured to a statistical accuracy of better than 1%.

POTENTIAL LOSSES OF RADIOACTIVE MATERIAL

Because of the high vapour pressure of cyclohexane it is possible that losses of radioactivity may occur during the diffusion experiment. This could result in a serious error in the evaluation of the diffusion coefficient. The design of the crystal holder successfully stopped the transfer of radioactive material to other faces of the crystal. This possibility was tested for by removing the sides of the crystal before sectioning. No radioactivity was ever detected in this material.

The possibility of complete loss from the surface was tested by carrying out several experiments by the surface decrease technique.[9] In these experiments the screwed metal cap, which normally covered the crystal during the diffusion anneals, was replaced by a G.M. tube (Mullard MX148, window thickness 1–2 mg cm^{-1}). This was held tightly onto the flange (C) (Fig. 1) by a screwed ring. The surface activity was then monitored during the diffusion anneal.

Because of the low energy of the carbon14, β particles and the difficulty of measurement of the β particle self absorption coefficient, the errors involved in this technique are large. The diffusion coefficients calculated from these measurements are in reasonable agreement with those obtained by the sectioning method. For example

T °K	D Section cm^2 sec^{-1}	D decrease cm^2 sec^{-1}
241.7	8.3×10^{-9}	7.6×10^{-9}
228.7	10×10^{-10}	2×10^{-10}

It can therefore be assumed that there were little or no losses of radioactivity.

Results

The process of self diffusion under the non steady state conditions used in the experiments is described by Fick's law.

$$\partial c/\partial t = -D \cdot \partial^2 c/\partial x^2$$

The diffusion coefficient D, is obtained by fitting the experimental data to an integrated form of this equation. In the present experiment diffusion was followed from an initial layer 1 μ thick for distances of 100–300 μ into a crystal of total thickness 1 cm. This corresponds to diffusion from a very thin source into a semi-infinite solid. For this geometry the correct integrated form of Fick's equation is[10]

$$C(x,t) = Q/(\pi Dt)^{\frac{1}{2}} \cdot \exp - (x^2/4Dt)$$

where C is the concentration of diffusing material at a distance x into the crystal after time t and Q, the total amount of material deposited at $x=0$ at $t=0$. If this interpretation of the geometry of the diffusion couple is correct then a plot of $\log_{10} C$ versus x^2 should yield a straight line of slope $-\log_{10} e/4Dt$. The results of such a plot for several of the experiments is shown in Fig. 2. In all cases the plot is linear indicating that there is only one major diffusion process taking place in the solid.

Studies of the non-plastic organic crystal anthracene[4, 5] reveal the presence of two diffusion processes. One, a slow process, involving the greater part of the diffusing activity, is presumably bulk diffusion. The second which was extremely rapid, was attributed to diffusion along dislocation pipes in the solid. In the present case the latter process is absent. This is taken to indicate that plastic solids have a low dislocation content.

From the slope of the penetration profile the diffusion coefficients can be evaluated. The results are summarized in Table 1.

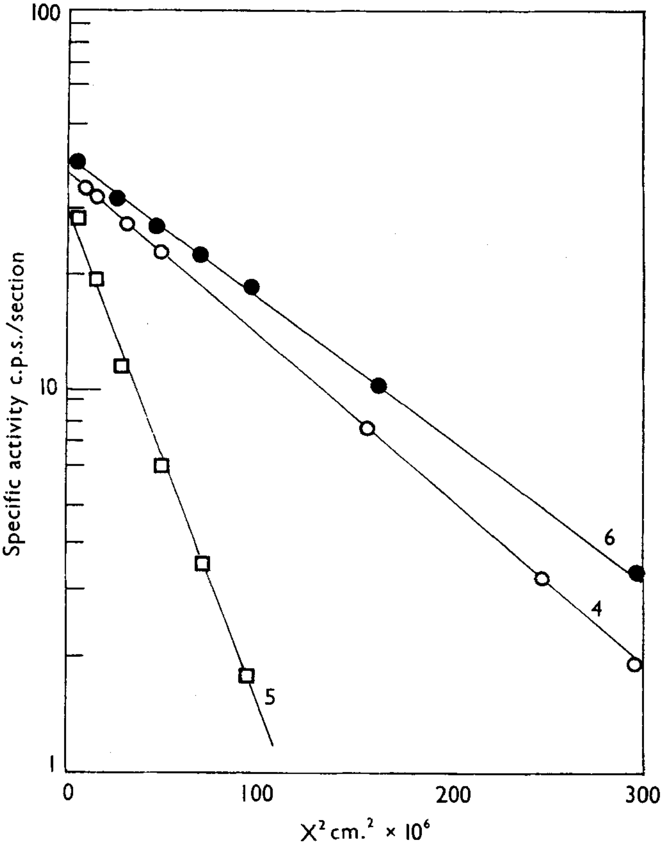

Figure 2. Activity profiles for self diffusion in cyclohexane. Experiment No. 4○, 5□, 6●.

A comparison of the data of Table 1 and Fig. 1 shows that the diffusion coefficient is independent of time and depth of diffusion. The values of the diffusion coefficient obtained for experiments carried out at 228.4° K are the same even though the annealing

TABLE 1 Diffusion Coefficients for Self Diffusion in Cyclohexane

Experiment no.	Diffusion period min	Diffusion coefficient $cm^2\ sec^{-1}$	Temperature °K
1	135	8.27×10^{-9}	241.7
2	213	2.37×10^{-9}	235.7
3	234	2.04×10^{-9}	234.2
4	450	0.94×10^{-9}	228.4
5	135	1.09×10^{-9}	228.4
6	728	6.75×10^{-10}	225.0
7	668	4.52×10^{-10}	223.2
8	1440	1.08×10^{-10}	215.7
9	2090	4.49×10^{-11}	210.6

times differ significantly. Consideration of the experimental data indicates that self diffusion in cyclohexane is an activated process. The data can be fitted by least mean squares analysis to an Arrhenius type equation

$D = D_0 \exp - \Delta H_d/RT$ (Fig. 3) with the parameters.

$D_0 = 3.9 \pm 3.8 \times 10^6\ cm^2 sec^{-1}$ and $\Delta H_d = 16{,}300 \pm 300\ cal\ mole^{-1}$.

If these results are compared with those of Andrew and Eades' n.m.r. study of cyclohexane[6] it will be seen that there is qualitative agreement. Diffusion rates in the plastic solids are extremely rapid, being 10^5 times more rapid at the melting point than in non plastic organic solids. It is not unreasonable then that diffusion has been observed in plastic solids by the n.m.r. technique whereas no such observation has yet been made for non plastic organic solids. There is however considerable discrepancy between the activation energy obtained in this tracer study and that obtained ($\Delta H_d = 8.5$ kcal) by n.m.r. A more extensive review of the relationship between radiotracer and n.m.r. studies of self diffusion in molecular solids has been given elsewhere.[22]

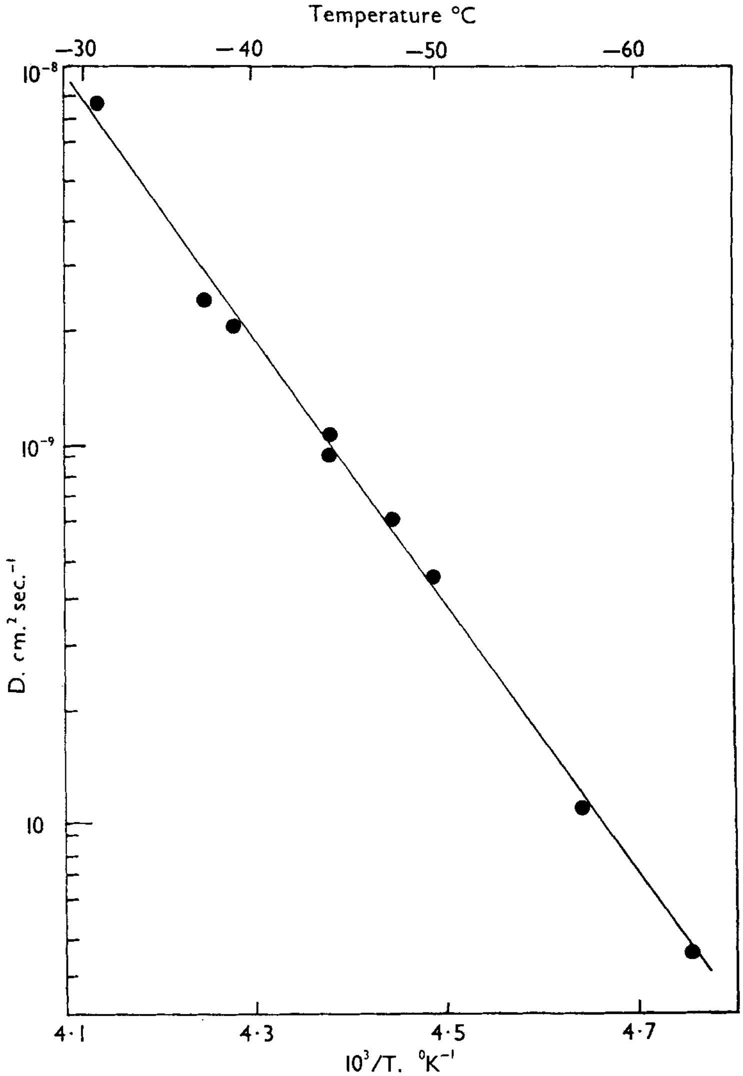

Figure 3. Temperature dependence of self diffusion in cyclohexane.

Discussion

Organic crystals are, in general, close packed solids. The crystal geometry is determined by the manner in which the bulky molecules fit together. In the plastic phase there is considerable rotational freedom indicating a less close packed structure. Comparison of molecular size and crystallographic dimensions[11] shows that the interstitial spaces in the lattice are too small to accommodate a molecule without distortion of the lattice. Diffusion by migration along the interstices is therefore impossible and motion by vacant lattice sites or some more complex mechanism is likely.

Thermodynamic consideration of the diffusion process has led to the formulation of an expression for the diffusion coefficient of the form:[12]

$$D = \gamma a^2 \nu \exp(\Delta S_d/R) \exp(\Delta H_d/RT)$$

where a is the jump distance and ν the jump frequency of the moving defect, γ a geometrical term dependent upon the lattice geometry and diffusion mechanism, and ΔS_d and ΔH_d the entropy and enthalpy of the diffusion process. If this expression is compared with the experimentally derived relationship it is seen that

$$D_0 = \gamma a^2 \nu \exp(\Delta S_d/R) = 3.9 \times 10^6 \,\mathrm{cm^2\,sec^{-1}} \quad \text{and}$$

$$\Delta H_d = 16.0 \pm 0.3 \,\mathrm{kcal\,mole^{-1}}.$$

The jump frequency can be approximated to the lattice vibrational frequency of the solid. No measurements of this parameter are available but a value can be calculated from the appropriate Debye characteristic temperature θ since $\nu \approx \frac{3}{4}\kappa\theta/\mathrm{h}$. Using the value of $\theta = 64°\,\mathrm{K}$ calculated from the Lindemann equation, which has been shown to give good agreement with experimental data for the rare gases,[13] it is found that $\nu \approx 1 \times 10^{11}\,\mathrm{sec^{-1}}$, a is equivalent to the lattice spacing 6.19×10^{-8} cm[11] and for most crystal structures $\gamma \approx 1$. Substituting these values in the above equation it is seen that $\Delta S_d = 41\,\mathrm{cal\,mole^{-1}\,deg^{-1}}$. In spite of any errors in evaluating ν, this entropy term is very large. It is far greater than those determined for self diffusion in face centred cubic metals in which a simple vacancy mechanism is well established[14] and probably indicates a diffusion process in which a number of molecules are involved.

The enthalpy of activation is the sum of two terms, the enthalpy of formation, ΔH_f, and the enthalpy of migration ΔH_m of the defect. No direct measurements of either of these quantities have yet been made for organic solids. Theoretically, it has been shown that for a molecular solid the enthalpy of formation of a vacancy should be approximately equal to the lattice energy of the solid.[10] This is the energy which would be required to abstract a molecule from a lattice site and replace it on the surface; the assumed mode of formation of a Schottky defect. Specific calculations of this term have been made for solid argon.[16] Experimental evidence is also available for this solid as a result of specific heat studies.[15] The results of these calculations indicate that for argon, $\Delta H_f \approx 1\text{–}1.4$ times the latent heat of sublimation. This confirms the above proposal. Since argon is a plastic solid with a face centred cubic lattice it is perhaps not unreasonable to assume that a similar state of affairs will hold for cyclohexane. The lattice energy of cyclohexane is 10 kcal mole^{-1}, which can therefore be regarded as a lower limit to the enthalpy of diffusion. It has been shown for metal systems that the enthalpy of migration of a vacancy is often of the same order, but less than the enthalpy of formation.[17] If the defects behave in much the same manner in molecular solids as in metals then the value for the diffusion enthalpy obtained in the present study is not unreasonable if diffusion proceeds by a vacancy mechanism. This would not however account for the high pre-exponential factor since, for face centred cubic metal systems, $D_0 \approx 0.1\text{–}1\,\mathrm{cm^2 sec^{-1}}$....[14]

It has been suggested[15] that, following the formation of a vacant lattice site in a molecular crystal, a relaxation of the surrounding molecules into the free space will occur. Such a proposal is very reasonable if the weak intermolecular binding forces in these molecular solids are considered. As a result of this weak bonding the gains in energy resulting from the relaxation will be small.[18] The enthalpy of formation of the relaxed vacancy would thus be approximately equal to the lattice energy of the solid. The defect would be a small disordered region in the solid which would probably involve at least the twelve nearest neighbours and the eight next nearest neighbours. Even allowing for lattice contraction following the relaxation (it is proposed that the excess volume due to the formation of this defect will be approximately 50% of the original vacancy void), such a region of twenty or more molecules will have a density more like that of the liquid than the solid.

Nachtrieb and Handler[19] have proposed such a defect to account for self diffusion in the alkali metals. These authors envisage that the solid contains liquid-like regions. Diffusion takes place by the melting and freezing of one or two molecules at a time with an activation energy of about the latent heat of fusion. Within the relaxion, as the authors term the defect, molecules move in a co-operative movement as in the liquid state. The enthalpy of migration of the defect will be equal to that of diffusion in the liquid state, $\Delta H_m \approx 4.57\,\mathrm{kcal\,mole^{-1}}$.[20] Since the relaxed vacancy will not be in a perfect liquid-like state this can probably be regarded as a minimum value. Thus $\Delta H_d \approx \Delta H_f + \Delta H_m \approx 10 + 4.6 = 14.6\,\mathrm{kcal}$, which is in reasonable agreement with the experimentally derived value.

In such a defect with many polyatomic molecules taking part in the diffusion process a high entropy of activation and hence pre-exponential factor would be expected. The approximate number of molecules associated with the defect and also the concentration of these defects in the lattice can be determined from Nachtrieb's analysis of the formation of the defect. Since in the extreme case motion proceeds via liquid-like relaxions the process must be like diffusion in a restricted liquid. The diffusion coefficient will therefore be dependent upon the number of liquid-like regions, i.e. the molecule will move rapidly whilst in the liquid-like region but will be otherwise stationary. Thus $D_{\mathrm{solid}} = XD_{\mathrm{liquid}}$ where X is the fraction of the total lattice present in relaxions. Now $X = A\exp-(\Delta G_f/RT)$ where A is a constant and ΔG_f the free energy of formation of the relaxion. It has been suggested that the free energy of formation of a n molecule disordered cluster in a solid will be[19]

$$\Delta G_f = nL/(1-T/T_m)$$

where L is the latent heat of fusion and T_m the melting temperature of the solid. Thus:

$$D_{\text{solid}} = D_{\text{liquid}} A \exp\left[-nL/(1-T/T_m)\right]$$

which can be rearranged to give

$$D_{\text{solid}} = D_{\text{liquid}} A \exp(nL/RT_m) \exp - (nL/RT)$$

and hence

$$\Delta S_f = nL/RT \qquad \text{and} \qquad \Delta H_f = nL.$$

ΔS_d as measured will be comprised of two terms, one for the motion ΔS_m the second for the formation ΔS_f of the defect. Since $D_{0\,\text{liquid}} = 30 \times 10^{-3}\,\text{cm}^2\text{sec}^{-1}$,[20] and $D_{0\,\text{solid}}$ $3.9 \times 10^6\,\text{cm}^2\text{sec}^{-1}$ the contribution of ΔS_m to the overall pre-exponential factor will be small and we can equate $\Delta S_d \approx nL/T_m$ or $\Delta S_d \approx n\Delta S_{\text{fusion}}$. The entropy of fusion of cyclohexane is $2.2\,\text{cal}\,\text{mole}^{-1}\text{deg}^{-1}$,[2] and $\Delta S_d = 41$ cal $\text{mole}^{-1}\text{deg}^{-1}$, hence $n = 20$. This is the number of nearest and next nearest neighbours in the lattice but since only partial melting will occur the defect is probably more extensive than this.

If N_R is the fractional number of relaxions in the lattice, then $N_R = X/n = 1/n \cdot D_{\text{solid}}/D_{\text{liquid}}$. A comparison of the self diffusion coefficients in the solid state with the data for self diffusion in the liquid state extrapolated to lower temperatures will give the relaxion concentration. Studies of self diffusion in cyclohexane in the temperature range $-5°$ C to $5°$ C using an exchange technique indicate that self diffusion proceeds via the same mechanism to within 1.5° of the melting point.[21] It is therefore reasonable to use the extrapolated data from the present experiment for this calculation. Several results are given in Table 2 for $n = 20$.

The values obtained are much higher than those for metal systems where defect concentrations of the order of 10^{-4} at the melting point are usually found. These values are however in reasonable agreement with estimates of the concentration of defects in plastic crystals (0.1–1 %) proposed by other workers.[11, 15] The only reliable data[23] indicate that the maximum concentration of defects will be less than 2 mole %. According to our calculation,

TABLE 2 Variation of Defect Concentration with Temperature

Temperature	D_{Solid} cm² sec⁻¹	D_{Liquid} cm² sec⁻¹	X	N_R mole fraction
279.7	7.36×10^{-7}	7.98×10^{-6}	9.2×10^{-2}	4.6×10^{-3}
273.2	3.49×10^{-7}	6.47×10^{-6}	5.4×10^{-2}	2.7×10^{-3}
241.7	8.27×10^{-9}	2.19×10^{-6}	3.8×10^{-3}	1.9×10^{-4}
223.2	4.52×10^{-10}	9.93×10^{-7}	4.6×10^{-4}	2.3×10^{-5}

at 0° C the concentration $N_R = 2 \times 10^{-3}$. If it is accepted that the defect contains twenty molecules, then approximately 2% of the crystal lattice will be in a disordered state. In such a highly disordered system it is not surprising to find a considerable degree of plasticity provided that the flow is diffusion controlled. The relationship between self diffusion and plastic flow is currently under study.

Acknowledgments

The authors wish to express their grateful thanks to the Science Research Council for the award of a studentship to G.M.H. and a grant for the purchase of apparatus to J.N.S.

REFERENCES

1. Timmermans, J., *J. Phys. Chem. Solids* **18**, 1 (1961).
2. Staveley, L. A. K., *Ann. Rev. Phys. Chem.* **13**, 351 (1962).
3. Andrew, E. R., *J. Phys. Chem. Solids* **18**, 9 (1961).
4. Sherwood, J. N. and Thomson, S. J., *Trans. Faraday Soc.* **56**, 1443 (1960).
5. Lee, C. H., Kevorkian, H. K., Reucroft, P. J., and Labes, M. M., *J. Chem. Phys.* **42**, 1406 (1965).
6. Andrew, E. R. and Eades, R. G., *Proc. Roy. Soc.* **216A**, 398 (1953).
7. Hood, G. M. and Sherwood, J. N., *Brit. J. Appl. Phys.* **14**, 215 (1963).
8. Tammann, G., *Z. Anorg. Chem.* **182**, 289 (1929).
9. Steigman, J., Shockley, W., and Nix, F. C., *Phys. Rev.* **56**, 13 (1959).
10. Jost, W., *Diffusion* (Academic Press, New York, 1960), p. 116.

11. Dunning, W. J., *J. Phys. Chem. Solids* **18**, 21 (1961).
12. LeClaire, A. D., *Progress in Metal Physics* **4**, 306 (1953).
13. Clusius, K., *Z. Phys. Chem.* (*Leipzig*) **B31**, 459 (1935).
14. Lazarus, D., *Solid State Physics* **10**, 116 (1960).
15. Flubacher, P., Leadbetter, A. J., and Morrison, J. A., *Proc. Phys. Soc.* **78**, 1449 (1961).
16. Kanzaki, H., *J. Phys. Chem. Solids* **2**, 24 (1957).
Nardelli, G. F. and Terzi, N., ibid. **25**, 815 (1964).
17. Shewmon, P., *Diffusion in Solids* (McGraw Hill, New York, 1963), p. 74.
18. Foreman, A. J. E., *Phil. Mag.* **8**, 1211 (1963).
19. Nachtrieb, N. H. and Handler, G. S., *Acta. Met.* **2**, 797 (1954); *J. Chem. Phys.* **23**, 1187 (1955).
20. McCall, D. W., Douglass, D. C., and Anderson, E. W., *J. Chem. Phys.* **31**, 1555 (1959).
21. Klimecki, W. J. and Sherwood, J. N. Unpublished work.
22. Hood, G. M. and Sherwood, J. N., *J. Chim. Phys.* to be published.
23. Higgins, P. F., Ivor, R. A. B., Staveley, L. A. K., and Virden, J. J. des C., *J. Chem. Soc.* 5762 (1965).