MOLECULAR FREEDOM IN SOLID SOLUTIONS OF HYDROCARBONS: SOME OBSERVATIONS ON POSSIBLE CAUSES OF SELF-DIFFUSION

J. G. Aston

The Pennsylvania State University, State College, Pennsylvania, U.S.A.

INTRODUCTION

Crystals of complex molecules which are highly spherical in shape have unusual properties for a considerable range of temperature below the melting point, as was first recognized by J. Timmermans who called such compounds " molecules globulaires ". While the melting point is sharp, the condensed phase below the melting point is not crystalline in the strict sense of the word.

The reflections of X-rays from the planes are much more diffuse than the reflections from the planes of the usual crystal[2, 3]. However, their reflections indicate a highly symmetrical arrangement of the centres of gravity of the molecules.

It has now been shown that in such crystals the molecules are more or less free to rotate and that there is also self-diffusion as in liquids. For this reason this writer prefers to call them plastic crystals (not to be confused with *liquid* crystals).

Because of the mobility in plastic crystals, " molecules globulaires ", when in such a state, are mutually soluble. The present paper compares the properties of the solid solutions formed in the plastic crystal with the properties of the components in an attempt to throw further light on the origin of their peculiar properties.

PROPERTIES OF PURE PLASTIC CRYSTALS (ONE COMPONENT)

Phase changes

On cooling plastic crystals to low temperatures they undergo one or more transitions in which rotation and migration stop. Examples of such transitions are given in *Table 1*, where the corresponding latent heat is given below the temperature. It should be noted that the plastic crystals in all cases have sharp, well defined, melting points with considerable heat of fusion. However, sometimes they pass into a phase which is quite analogous to a glass. Such a condition will be discussed later.

The transitions may be of the first order or of the second (or higher order). It is an almost universal rule that if the molecule approximates spherical symmetry (*e.g.* methane, carbon tetrachloride, *etc.*) sufficiently closely, the transition in which most of the rotation is lost will be second order. The corresponding transition will be first order if the molecule approximates an

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Table 1. Data on solid and liquid phases of " molecules globulaires "

Compound	Measured line widths*			Calculated line widths (G)		Transition temperatures (°K)		Melting temp. (°K)	ΔS of fusion (cal °C⁻¹ mole⁻¹)
	I	II	III†	Rigid	Rotating	Lower	Upper		
Methane[6]	~7(a)	~7 → 0(a)	—	16(a)	14(a)	20(S) 157‡	—	90·0	2·47
Carbon tetrafluoride[7]	~13(b)	~0·5 → 0(b)	—	12(b)	< 1·50(b)	76(S) 354‡	—	89·5	1·84
Perfluoroethane[8]	~15(b)	~1·2 → 0(a)	—	> 7·5(b)	—	104(S) 893‡	—	173·0	3·70
Carbon tetrachloride[9]	—	—	—	—	—	225(S) 1095‡	—	250·3	2·40
Tetramethylmethane[8, 10]	2·5(a)	2·5(a)	—	—	—	140(S) 616‡	—	256·0	3·03
Cyclohexane[11, 12]	26 → 6·4(b)	1·4(b)	—	—	—	186(S) 1598‡	—	279·8	2·24
2,2-Dimethylbutane[13]	9(a)	2·3 → 0·4(a)	0·4(a)	—	—	127(F) 1289‡	141(F) 68‡	174·2	0·79
Cyclopentane[14]	26(b)	0·8 → 0·2(b)	0·3 → 0(b)	28·0(b)	1·7(b)	122(F) 1165‡	138(F) 83‡	179·7	0·80
2,3-Dimethylbutane[13a]	~9(a)	—	—	—	—	136(F) 1552‡	—	145·2	1·32
tert-Butyl chloride[15]	4·0(a)	4·0(a)	0·5(a)	16(a)	—	183(S) 410‡	220(S) 1390‡	248·2	1·90

* Width at half the (a) peak height (G), or (b) second moment (G²).
† I denotes solid phase stable at low temperature.   II and III denote solid phases respectively stable at increasingly higher temperatures.
‡ Heat of transition in cal/mole.

oblate spheroid (*e.g.* cyclopentane) or is pear-shaped (*e.g.* 2,2-dimethyl-butane). In *Table 1* the transition temperature is marked (F) if the transition is first order and (S) if the transition is second order.

Dielectric constants of the phases

It was early recognized by Smythe and co-workers[4] that when a liquid composed of polar molecules froze to yield a plastic crystal, the dielectric constant suffered no sharp fall analogous to that which occurs when rotation is not possible. Indeed, later they devised an apparatus for measuring dielectric constants and heat capacities simultaneously[5]. With this, they showed, for example, that *tert*-butyl chloride had two transitions, the upper being second order and with the higher heat. On cooling it was at the upper transition that the sharp fall in dielectric constant occurred.

Nuclear magnetic resonance line broadening

Gutowsky and Andrew together with their co-workers have studied the effect of rotation in the solid state on the shape of the nuclear magnetic resonance absorption line. The observed shapes may be compared with values calculated from theory. A line which is broad below a rotational transition will become narrow above the transition. However, a line may become narrow owing to flipping of methyl groups over the barrier hindering rotation. Also, as in the case of methane, the arrangement of the proton spins in the non-rotating form may be such as to produce a line so narrow that the rotation of the molecule above cannot produce significant narrowing. Thus, the shape of the nuclear magnetic resonance line is not always as obvious a criterion of rotation as the dielectric constant. The method of nuclear magnetic resonance has the advantage that it can be used with non-polar molecules and that the measured line shape can be compared with one calculated theoretically on the basis of postulated models. *Table 1* summarizes the transition temperatures and the nuclear magnetic resonance line width for a number of solids.

## Self-diffusion in plastic crystals and its origin

Comparison of measured line shapes with those calculated from theory has shown that cyclopentane after passing through the lower transition undergoes self-diffusion in the crystal, as well as rotation, whereas carbon tetrafluoride shows no evidence of self-diffusion till the melting point is reached, while methane only shows evidence of self-diffusion when the rotating crystal is close to the melting point. In the case of cyclohexane the nuclear magnetic resonance shows rotation but no self-diffusion immediately above the rotational transition. Half-way towards the melting point only does the line narrow to values which indicate self-diffusion. Inspection of models makes it evident that the envelope over the general shape of cyclopentane is roughly an oblate spheroid, whereas for cyclohexane a similar envelope is almost spherical. The nuclear magnetic resonance measurements[15] on *tert*-butyl chloride confirm the conclusions from the dielectric constant measurements, namely that it is at the upper second order transition that most of the rotation begins.

The graph of heat capacity as a function of temperature for cyclopentane which is given in *Figure 3* shows that the first transition, where most of the rotation sets in, is first order, as also is the second.

It should be noted that in the usual case the heat capacity curve for a liquid at the melting point is considerably above that of the crystal immediately below the melting point when the crystal is a true crystal. Thus, in the case of a first order rotational transition the heat capacity of the rotating phase immediately above the rotational transition should be considerably higher than that of the non-rotating phase.

The argument for this is that apparently where the transition is first order (oblate spheroidal or pear-shaped molecules) rotation and migration set in simultaneously producing a sufficiently high degree of co-operation to make the transition first order. Thus, the situation is similar to that at the melting point of an ordinary crystal. The heat capacity curve of cyclopentane shown in *Figure 3* is in agreement with this prediction.

When the transition is second order (almost spherical molecules) except for the immediate neighbourhood of the transition, the curve for the rotating solid is almost a continuation of that of the non-rotating solid. In the case of almost spherical molecules it is only rotation that sets in at the rotational transition. There is no translation; thus, the transition is not as sharp as when self-diffusion sets in simultaneously.
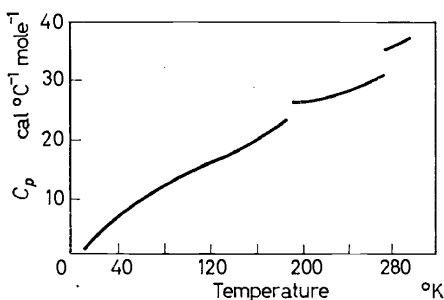
Figure 1. The heat capacity of cyclohexane
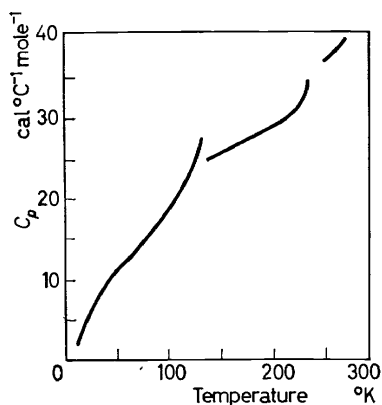
Figure 2. The heat capacity of tetramethylmethane

Cyclohexane is a good example. The curve of heat capacity against temperature shown in *Figure 1* has a transition. On the low temperature side of the transition the abnormal rise in the heat capacity is evident, although not very pronounced. The striking thing is that the heat capacity for the solid above the transition is almost a continuation of that below. This is in accord with the nuclear magnetic resonance data. Comparison with the corresponding heat capacity curve of tetramethylmethane given in *Figure 2* indicates that cyclohexane is similar to tetramethylmethane, whose molecules have a spherical envelope, and cyclopentane is not similar (see *Figure 3*).

The entropies of fusion given in the last column in *Table 1* are a striking confirmation of these conclusions. Monoatomic crystalline solids, on fusion,

gain the communal entropy of R. Compounds with no rotational transitions (where rotation sets in on melting) have an entropy increase several times R, because they gain rotational as well as translational entropy on fusion. Examples are n-butane and n-pentane whose entropies of fusion are 8·3 and 14·0 cal °K^{-1} mole^{-1}. Compounds with second order rotational transitions have an entropy of fusion of about R, which is the increase in communal entropy, whereas those showing first order transitions have considerably lower entropy of fusion. When a solid is rotating, it only has to gain its communal entropy of fusion. If, on the other hand, the solid has some translational freedom as well as fully excited rotation, some of the communal entropy has already been gained before melting. Thus the entropy change is smaller than R.
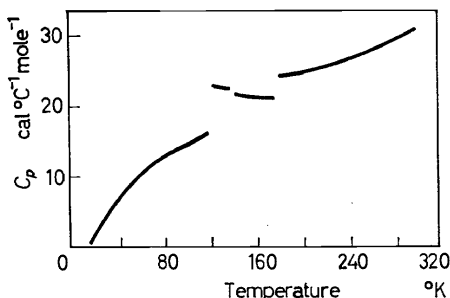

Figure 3. The heat capacity of cyclopentane

SOLID SOLUTIONS AND MIXTURES
Systems with spherical molecules

It is natural to expect from what has just been said about spherical molecules, that krypton, whose atoms have about the same atomic diameter as the molecules of methane, would form solid solutions with it. This is indeed the case. It would also be expected that the truly spherical nature of the krypton diluting, atoms would make it easier for methane molecules to rotate. For pure methane, when one molecule starts to rotate it is easier for another molecule to do so. If krypton is present there is no similar rotation of krypton atoms to assist. Thus, the effect of krypton should be
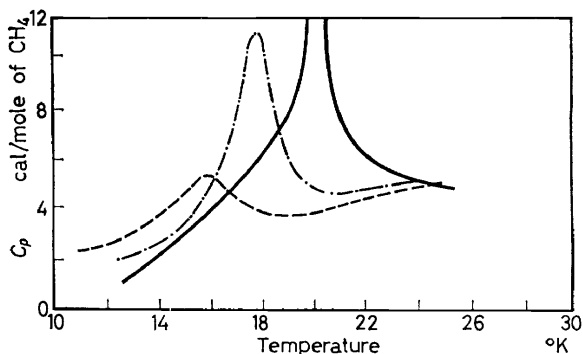

Figure 4. Methane diluted with krypton: — O%Kr; — · — 7·45%Kr; – – – 15·60%Kr

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to decrease the degree of co-operation and to make the transition of higher order than second. Eucken and Vieth[16] have studied the heat capacities of solutions of krypton in methane. Their results, which are shown in *Figure 4*, constitute a striking verification of the predictions.

A further verification of the factors causing rotation in the solid state is obtained by examining the heat capacities of methane adsorbed on a surface. Steele[17] has found that the transition is present in methane down to a coverage of two layers. At this coverage the λ transition has only been lowered by 0·3°. This effect is understandable when one notes that below 17°K the heat capacities for less than two layers are considerably smaller than those of the systems showing lambda transitions. This means that the molecules are rotating more or less freely in the monolayer (classical heat capacity $R/2$, as compared with R for vibration). For two layers this is presumably true for the outer one. The lambda point above two layers involves only rotation in the inner layers, which should not differ much from that in the bulk.

Incomplete nuclear magnetic resonance measurements on methane[18] have been carried out in the writer's laboratory for the purpose of supplementing the heat capacity data. While the accuracy of the data at the low coverages is questionable, the data at four monolayers seem to verify the conclusions from the heat capacities. These measurements are, of course, being repeated.
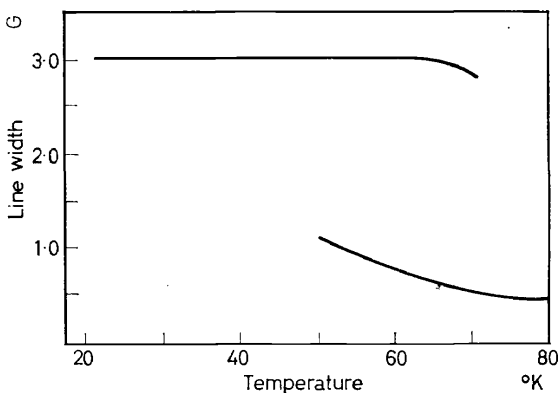
Figure 5. Line width *versus* temperature for one monolayer of CF_4 on TiO_2

Nuclear magnetic resonance studies have been made on carbon tetrafluoride adsorbed on high-area titanium dioxide[7].

In *Figure 5* are shown graphs of the line width (at half the peak height) *versus* temperature of the narrow and broad components of the line for one molecular layer on the surface. The narrow component is due to rotation which does not cease above 20°K. This confirms the fact that in order to prevent rotation at any temperature a full complement of nearest neighbours in all three dimensions as in a crystal is necessary. A full complement of neighbours in a plane will not do. This confirms results obtained for diatomic gases at Oxford[19, 20].

Carbon tetrachloride and *tert*-butyl chloride form a continuous series of solid solutions[4] with a minimum in the melting point diagram at 50 mole-

per cent. The rotational transition for the 50 mole-per cent solid solution is at 231°K which is above the upper rotational transition of *tert*-butyl chloride, as well as above the rotational transition of the carbon tetrachloride. In this case there is no reason to expect that rotation of either component would be easier in the mixture. The fact that there is a minimum in the melting point diagram at 50 mole-per cent would lead one to expect a some-what closer packing in the rotating solid solution than in the rotating crystal of either component and hence a somewhat higher temperature for the rotational transition.

Systems with non-spherical molecules

Two binary systems involving non-spherical molecules have been inves-tigated, namely: (A) 2,2- with 2,3-dimethylbutane[22] and (B) 2,2-dimethyl-butane–cyclohexane[23, 21].

In the case of the first of these systems there is a maximum in the melting point diagram at 0·40 mole 2,3-dimethylbutane and 0·60 mole 2,2-dimethyl-butane. This mixture has a sharp melting point and presumably indicates some preferred crystal arrangement (complex).

The heat capacity[22] is shown in *Figure 6* along with the N.M.R. line width. The melting point is sharp. Below the melting point the heat capacity curve resembles that of a glass, there being a slight peak after the rapid rise in heat capacity characteristic of the softening of a glass. This peak is accompanied by a decrease in N.M.R. line width from 8 to 2 gauss. The entropy change on melting is[22] 1·61 cal/°K per mole of mixture (*i.e.* 0·40 mole 2,3-dimethylbutane and 0·60 mole 2,2-dimethylbutane). This is considerably higher than the normal entropy of fusion of either component. On the basis of the qualitative correlation of the pure components one would suspect that the rotational transition would be second order. Unfortunately no rotational transition is observed owing to the supercooling to a glass.
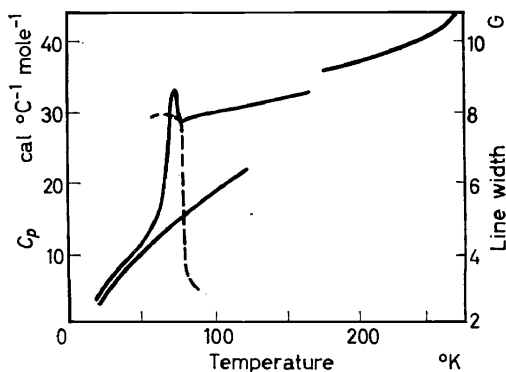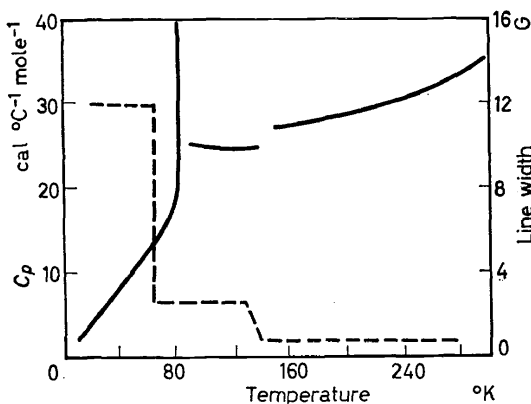

Figure 6. Heat capacity and N.M.R. line width of 0·4 mole 2,3–dimethylbutane and 0·6 mole 2,2–dimethylbutane: — heat capacity; – – line width

The data on the 2,2-dimethylbutane–cyclopentane system definitely confirm this conclusion. In this system there is a maximum in the melting point curve at 0·33 mole 2,2-dimethylbutane and 0·67 mole cyclopentane.

The heat capacity[23] curve for this mixture is shown in *Figure 7*. Here again the melting point is sharp. There is no tendency to supercool, and the rotational transition can be observed. In place of the two transitions for each component there is a single transition at 83°K. This transition is second order. The entropy of fusion is 1·45 cal/°K per mole of mixture (0·333 mole 2,2-dimethylbutane and 0·667 mole cyclopentane). This is considerably higher than the molal entropy of fusion for either of the components.

The width of the N.M.R. line as a function of temperature is also shown in *Figure 7*. There is a narrowing from 12 G to 3 G at about 65°K, where the abnormal rise in heat capacity preceeding the transition starts. This value of 3 G is of the order of that expected for rotating molecules with fixed centres. It is only near the melting point that the line narrows to 1 G, indicating self-diffusion.

Figure 7. Heat capacity and N.M.R. line width of 0·333 mole 2,2-dimethylbutane and 0·667 mole cyclopentane

The fact that the transition occurs at a temperature forty degrees below the lowest transition of either component indicates that there is some sort of favoured unit (complex) of 1 mole of 2,2-dimethylbutane to 2 moles of cyclopentane which rotates in the crystal more easily than does either component. This unit would be expected to have high symmetry, to rotate with such ease. This is in keeping with the fact that the transition is second order. The fact that the average entropy of fusion is nearer R per component molecule than that for either component means that the 2,2-dimethylbutane and cyclopentane molecules gain almost their full communal entropy on melting. This indicates little self-diffusion in the rotating crystal, in keeping with the N.M.R. data. In molecules with almost spherical envelopes there is little self-diffusion.

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