*Entropy and Molecular Motion in the Condensed Phases of Tetrahedral Molecules**

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Much attention has been paid to the molecular motion in a class of compounds which were named plastic crystals by Timmermans,[1] who illustrated that crystals composed of molecules more or less spherical in shape have small entropies of fusion (less than 5 e.u.) and exhibit plasticity below their melting point. Evidence has been accumulated by studies of X-ray diffraction, nuclear magnetic resonance, dielectric absorption, etc. to indicate that molecules in the plastic crystals are capable of rotational motion, if not completely free. Since the entropy is a measure of the degree of disorder, it will also give us some clue to the state of molecular motion in solids, a clue which would complement the deductions from other types of experiments.

Plastic crystals usually have a transition accompanying a large entropy change comparable to or greater than the entropy of fusion. The sum of the two entropies is close to what one expects from Walden's rule (13 e.u.).[2] This forms the basis of the interpretation that such crystals melt in two successive processes; the rotational degrees melt at the transition point, while the translational degrees melt at the triple point. However, this is an over-simplified model, as is evident from detailed studies. For example, the X-ray diffraction[3] of Si_2Me_6 indicates that the molecular axis is statistically oriented along one of the body-diagonals of the cubic unit cell; therefore, the disorder is not considered perfect. The nuclear magnetic resonance study of CMe_4 by Gutowsky et al.[4] found the potential barrier hindering molecular reorientation in the plastic phase (called phase I hereafter) to be 1.0 kcal./mol.; it also showed that the molecular rotation is not free. One should then be able to see some consequences of the hindrance of rotation in the thermodynamic quantities.

A comparison of the entropy of fusion of, say, face-centered cubic carbon tetrachloride (2.401 e.u.) with that of an inert gas solid (3.395 e.u. for argon) provides a clue to this problem. The fact that the fusion of argon requires a larger entropy change than does the fusion of carbon tetrachloride is just the contrary to what one would anticipate on the basis of the over-simplified model. The situation may conveniently be visualized in terms of diagrams of the degree of disorder in different phases; such diagrams are drawn in Fig. 1

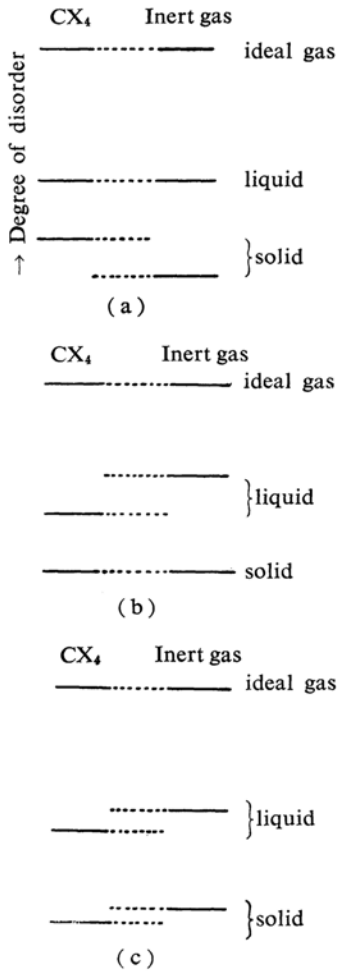

Fig. 1. A schematic representation of the degree of disorder in different phases of CX_4 type molecules and inert gases. (a) and (b) are extremely idealized situation, (c) is the actual situation.

* Presented before the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

1) J. Timmermans, *J. chim. phys.*, **35**, 331 (1938).
2) P. Walden, *Z. Elektrochem.*, **14**, 713 (1908).
3) Y. Chatani, unpublished.
4) E. O. Stejskal, D. E. Woessner, T. C. Farrar and H. S. Gutowsky, *J. Chem. Phys.*, **31**, 55 (1959).

on the analogy of the more familiar energy-level scheme. The fact that carbon tetrachloride has a smaller entropy of fusion than an average inert gas solid may be accounted for in two extreme ways: (a) carbon tetrachloride molecules would move more freely than argon in the solid state if fusion in general could remove all the positional and orientational constraints in the solid to give any liquid the same degree of disorder (see Fig. 1a), and (b) the motion of carbon tetrachloride molecules would be less free in the liquid if both carbon tetrachloride and argon possess the same degree of disorder in the solid just before they melt (Fig. 1b). Of course, there are other possibilities, such as an intermediate between those two extremes, in which both of the carbon tetrachloride "levels" are displaced with respect to the corresponding argon "levels". In what follows, the actual level scheme will be shown to correspond to the one given in Fig. 1c. It will also be shown that the displacement of the solid levels may be explained by the hindered rotation of carbon tetrachloride molecules in the solid and that the displacement of the liquid levels may be explained by a simple cluster model of the carbon tetrachloride liquid. Effective values of the hindering potential barriers were derived for carbon tetrafluoride, carbon tetrachloride and neopentane in connection with a consideration of the possible orientations of molecules in crystals.

The Entropy of Sublimation and Molecular Motion in Solid. — Let us take the state of ideal gases at the triple points as the state of perfect disorder; neither the solid nor the liquid state is by itself in general a state of a well-defined degree of order. The degree of disorder in a solid at the same temperature will then be quantitatively expressed by its entropy of sublimation at the triple points. Since we are interested in the difference in behavior between inert gas molecules (suffix 1) and tetrahedral molecules (suffix 2), we shall fix our attention upon the difference in the entropies of sublimation:

$$(\Delta S_2-\Delta S_1)^{S\to G}=(T_2{}^G-T_2{}^S+R_2{}^G-R_2{}^S)-(T_1{}^G-T_1{}^S) \quad (1)$$

where T and R are the entropies of the translational (including configurational) and the rotational degrees of freedom respectively, and where the superscripts G and S refer to the ideal gas at atmospheric pressure and at the solid states respectively. Here it has been assumed that the intramolecular contribution to the entropy remains unaltered in the process of the phase change involved. A rearrangement of Eq. 1 gives

$$R_2{}^G-R_2{}^S=(\Delta S_2-\Delta S_1)^{S\to G}+\{(T_1{}^G-T_1{}^S)-(T_2{}^G-T_2{}^S)\} \quad (2)$$

We now assume that the bracketed term on the right hand side may be disregarded if we choose a hypothetical inert gas whose molecular weight is the same as for the particular CX_4; in other words, we assume that the degree of disorder is the same with respect to the configuration and motion of the molecular centers of mass, the molecular masses and the crystal structures being identical.

Table I lists the thermochemical values*1 relevant to the present calculation. A value of $\Delta S_1{}^{S\to G}$ was read off Fig. 2 for an appropriate molecular weight. The $(R_2{}^G-R_2{}^S)$ value thus obtained can be interpreted in various ways. An obvious way is that the rotational motion of CX_4 molecules is restricted in the solid state. The motion could either be a reorientation or a hindered rotation.*2

TABLE I. TRIPLE POINTS AND ENTROPY CHANGES (e.u.) AT THE TRIPLE POINTS

	Triple point, °K	$\Delta S^{S\to L}$	$\Delta S^{L\to G}$	$\Delta S^{S\to G}$	Ref.
Ne	24.57	3.26	16.23	19.49	5
Ar	83.810	3.395	18.15	21.54	6,13
Kr	115.776	3.386	18.38	21.77	7,25
Xe	161.3	3.400	19.216	22.616	8
CH_4	90.66	2.474	18.76	21.23	9
CF_4	89.47	1.87	24.81	26.68	10
CCl_4	250.3	2.401	24.52	26.92	11
CMe_4	256.53	3.03	20.70	23.73	12

*1 The entropies of vaporization at the triple points were computed from literature values of the entropy of vaporization at the boiling point (or at 25°C) and of the heat capacities of liquid and ideal gases. The entropies were corrected for the non-ideality of the gas and for the work of expansion from the triple point pressure to the standard pressure. The value for carbon tetrabromide was not obtained because its liquid heat capacity is not completely known.

*2 It seems that there has been some confusion or an indiscriminate use of the terms, reorientation and hindered rotation; thus it would be appropriate to define the words here, at least for the present purposes. By hindered rotation, it is meant that the molecules can rotate in one or the other direction over potential barriers with an average total energy sufficient to surmount the barrier; the rotational energy level is, therefore, above the top of the hindering barrier, On the other hand, if the average total energy is numerically less than the hindering potential, the molecule will normally oscillate in the potential well, with only occasional go-over when the molecule has acquired greater energy through statistical fluctuation. This we call reorientation. The frequency of the reorientation depends on the temperature and on the height of the potential barrier.

5) F. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," NBS Circular 500 (1952), p. 543.
6) K. Clusius and A. Frank, *Z. Electrochem.*, **49**, 308 (1943).
7) K. Clusius, A. Kruis and F. Konnertz, *Ann. Physik*, **33**, 642 (1938).
8) K. Clusius and L. Riccoboni, *Z. physik. Chem.*, **B38**, 81 (1938).
9) A. Frank and K. Clusius, ibid., **B36**, 291 (1937).

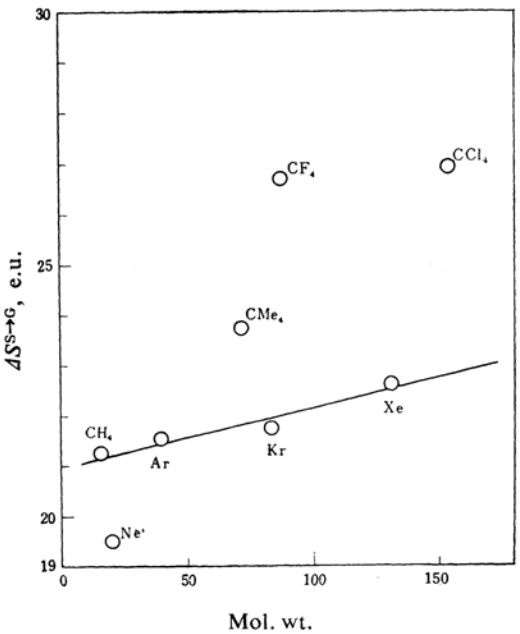

Fig. 2. Entropy of sublimation plotted versus molecular weight. A hypothetical inert gas of the same molecular weight is chosen to compare with a particular CX_4.

Our knowledge of the crystal structures of these compounds is not very complete. Their structure in the plastic phases is all face-centered cubic, at least with regard to the spatial arrangement of the center of gravity of the molecules; the one possible exception is carbon tetrafluoride, the structure of which is not yet known. It is reasonable, however, to assume that carbon tetrafluoride is isomorphous with carbon tetrachloride. The orientation of molecules in the lattice was not determined with certainty. For instance, the X-ray diffraction intensities from carbon tetrachloride[14] in its phase I can not be accounted for by a model of fixed molecular orientations, but they are appropriate to a model of rotating molecules even though the rotation is not perfectly free. For neopentane,[15] the temperature factor of the X-ray diffraction is so large that an almost free rotation of the molecules is suggested. The nuclear magnetic resonance experiments[16] (except carbon tetrachloride) give more direct information as to the mode of molecular motion in phase I (relative to X-ray studies), and it is strongly suggested that molecules are undergoing general rotation or three-dimensional reorientation (no distinction seems possible). Gutowsky[4] was able to derive the barrier height hindering the reorientation of the neopentane molecule as 1.0 kcal./mol. The crystal structure of phase II of these solids is even less well known. Mones and Post[15] reported that neopentane is weakly birefringent below the transition point and that it is probably tetragonal (close to cubic, however, $a_0=11.2$Å, $c_0=11.5$Å). It is generally agreed that methane is very close to cubic at lowest temperatures. Its zero-point configuration was studied by Nagamiya[17] and by James and Keenan[18]; the latter made a careful analysis of the stability of various orientations of molecules. Although James and Keenan's model for the structure of phase II of CD_4 is extremely idealized, their zero-point configuration is much more reliable*3 in the sense that it is the result of the self-consistent calculation of static lattice energy. We shall use this configuration as the basis of the present analysis.

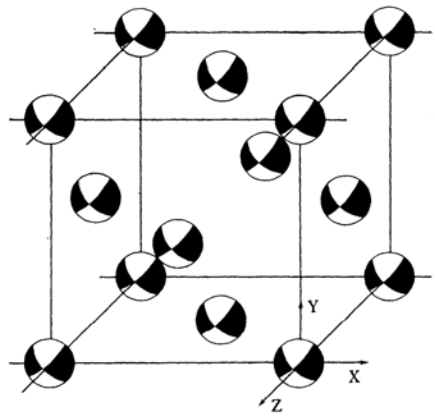

Fig. 3. Zero-point configuration of CD_4 crystal derived by James and Keenan, taken from Fig. 7 of Ref. 16. Black spots represent D atoms.

The James and Keenan structure for the phase III of CD_4 is reproduced from their paper in Fig. 3. We shall assume that this structure represents the features of the molecular orientational arrangement in all CX_4 molecules to be considered in this paper. In

10) A. Eucken and E. Schröder, ibid., **B41**, 307 (1938).
11) J. F. G. Hicks, J. G. Hooley and C. C. Stephenson, *J. Am. Chem. Soc.*, **66**, 1064 (1944).
12) J. G. Aston and G. H. Messerly, ibid., **58**, 2354 (1936); J. G. Aston, *Chem. Revs.*, **27**, 59 (1940).
13) P. Flubacher, J. Leadbetter and J. A. Morrison, *Proc. Phys. Soc.*, **A78**, 1449 (1961).
14) B. Post, *Acta Cryst.*, **12**, 349 (1959).
15) A. H. Mones and B. Post, *J. Chem. Phys.*, **20**, 755 (1952).
16) J. G. Aston, Q. R. Stottlemyer and G. R. Murray, *J. Am. Chem. Soc.*, **82**, 1281 (1960).

*3 Recently Savitsky and Hornig[19] cast, on the basis of infrared studies, some doubt on the James and Keenan structure, but their doubt is not considered definite either.
17) T. Nagamiya, *Prog. Theor. Phys.*, **6**, 702 (1951).
18) H. M. James and T. A. Keenan, *J. Chem. Phys.*, **31**, 12 (1959).
19) G. B. Savitsky and D. F. Hornig, ibid., **36**, 2634 (1962).

TABLE II. DERIVED PROPERTIES OF CX_4 MOLECULES

	Rotational entropy in solid R_2^S (e.u.)	Reorientation mechanism		Hindered rotation mechanism
		torsional freq. cm^{-1}	pot. barrier kcal./mol.	pot. barrier kcal./mol.
CH_4	6.67	—	—	—
CF_4	11.67	30.4	3.4	1.0
CCl_4	18.95	24.8	7.7	2.4
CMe_4	18.33	28.3	3.8	1.3

the James and Keenan structure, the centers of the mass of molecules form a face-centerd lattice and one of the molecular C_2 axes is parallel with one of the crystallographic axes, while the others make an angle of 45° with two other crystallographic axes. The structure of the plastic phase is, of course, related to this zero-point configuration, the latter, however, being tetragonal rather than cubic. The structure of Fig. 3 can be rendered as a cubic symmetry, and, at the same time, as a rotational disorder if the plastic phase structure is assumed to be a hybrid of three such configurations in which crystal axes are permuted. As a first approximation, we shall assume that molecular rotation is a superposition of three independent plane rotations; the potential barrier hindering the rotation thus lies at 90° from the orientation of the minimum potential energy in three directions, in an adiabatic approximation in which the orientations of neighboring molecules are fixed. Such tetragonality disappears at the transition point in accordance with the excitation of the molecular rotational degrees of freedom or reorientation. A Similar consideration will apply to other CX_4 molecules.

i) Reorientation Mechanism.—First we will consider a model in which molecules reorient themselves in order that the crystal may possess the cubic symmetry. Molecules are in the state of harmonic libration (torsional oscillation) of frequency in potential minima and occasionally jump over the potential barrier. There are two distinguishable configurations*4 per molecule which contribute to the entropy R_2^S, which now becomes

$$R_2^S = 3R\,[x\exp(-x)/\{1-\exp(-x)\} - \ln\{1-\exp(-x)\}] + R\ln 2 \qquad (3)$$

where $x = h\nu/kT$

*4 Starting with the zero-point configuration, in which two of the diad axes of neighbor molecules make an angle of 45° with, say, the b and c axes of the lattice, a central molecule has two distinguishable orientations. The cubic symmetry of the crystal lattice is then acquired if the neighbor molecules take three different orientations wihch are obtained by the permutation of the crystal axes, a, b, and c. The original zero-point configuration, therefore, appears at the probability of 1/3, and there are three permutations of the crystal axes. The total number of distinguishable configurations will thus be $(2\times1/3\times3)^N = 2^N$.

The values of ν and their corresponding potential barriers, V_0, were derived from $(R_2^G - R_2^S)$ by the use of Eq. 3 and $V = (1/2)V_0(1-\cos 2\theta)$ and are given in Table II. For methane, the $(R_2^G - R_2^S)$ is very close to zero, and, therefore, the molecules are rotating almost freely in phase I (at the triple point), in agreement with Staveley's analysis of the heat capacity.[20] There are no literature values available to compare with the ν and V_0 values derived here except for the ν of carbon tetrachloride in the low temperature phase, which was estimated to be 36.5~38 cm^{-1} by Gutowsky and McCall[21] from their measurements of chlorine nuclear quadrupole resonance frequencies as a function of temperature. The present value of 24.8 cm^{-1} for carbon tetrachloride is not unreasonable for the high temperature phase.

ii) Hindered Rotation Mechanism. — If one assumes the superposition of three plane rotators of CX_4 molecules in a solid in a potential field of the type

$$V = (1/2)V_0(1-\cos 2\theta) \qquad (4)$$

which is equivalent to assuming the rotation around the two-fold axes of a molecule, its contribution, R_2^S, to the entropy can be calculated by the help of Pitzer's table.[22] The values of the hindering potential, V_0, which correspond to the $(R_2^G - R_2^S)$ values for three degrees of freedom of rotation, are listed in Table II.

For the three compounds, carbon tetrafluoride, carbon tetrachloride and neopentane, the potential barrier in the reorientation mechanism is, as we have seen in Table II, comparable in magnitude with the heat of sublimation (2.4, 6.7 and 6.1 kcal./mol., respectively), and it is larger than the barrier for the hindered rotation mechanism by a factor of about three. Therefore, we consider that mechanism ii), the hindered rotation mechanism, is the more likely one. There is another reason for believing so: a consideration of the nuclear magnetic resonance of carbon tetrafluoride. Aston and others[16] showed that the

20) L. A. K. Staveley, *J. Phys. Chem. Solids*, **18**, 46 (1961).
21) H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **32**, 548 (1960).
22) K. S. Pitzer, "Quantum Chemistry," Constable and Company, Ltd., London (1953), p. 498.

rigid lattice width of the fluorine resonance absorption in carbon tetrafluoride is about 12 gauss, which narrows in two distinct steps, at 55~65°K and at the transition point. They suggested, on the basis of their calculation of second moments, that carbon tetrafluoride molecules begin to rotate first around their two-fold axis at about 55°K and then rotate about all axes at higher temperatures. Now it is of some interest to examine what consequences in the nuclear resonance may be anticipated if we apply the familiar equation of the absolute reaction rate theory[23]

$$\nu \approx (kT/h) \exp(-V_0/kT) \tag{5}$$

to derive the frequency at which the molecules would jump over the potential barrier, V_0. The substitution of $V_0=3.4$ kcal./mol. and $T=89.47$°K leads to $\nu \fallingdotseq 9.2\times10^3\ \mathrm{sec}^{-1}$. This value of ν indicates that the motional narrowing will not occur until higher temperatures (97°K) because the rigid lattice width, 12 gauss, corresponds to $4.8\times10^4\ \mathrm{sec}^{-1}$ for the fluorine nucleus[24]. On the other hand, $V_0=1.0$ kcal./mol. gives $\nu \approx 7\times10^{10}\ \mathrm{sec}^{-1}$, which is sufficiently rapid to cause motional narrowing; the narrowing would occur at 30°K if the same potential barrier height persisted at such a temperature.

The fore-going analysis gives support to the view that the rotation of tetrahedral molecules in their plastic phase is not free, except possibly in the case of methane.

A Model for Liquid Carbon Tetrachloride at Its Triple Point

It remains to be examined how the displacement (in Fig. 1c) of the "level" of carbon tetrachloride with respect to the inert gas liquid "level" can be explained. The model we will now present is perhaps one of the simplest, but yet, we hope, it represents the feature of the structure of liquid at the triple point. We shall here consider carbon tetrachloride as an example.

It may be assumed that liquid carbon tetrachloride consists of clusters (embryos of crystallites), each containing n molecules, and that the arrangement and motion of the centers of mass of clusters are in the same degree of disorder as in an inert gas liquid. The molar entropy of liquid carbon tetrachloride will, then, be

$$S_2^{\mathrm{L}} = \frac{1}{n}(T_2+R_2+C_2)_{\mathrm{cluster}} + \frac{1}{n}(3n-6)s_l + R_2^{\mathrm{L}} + I_2 \tag{6}$$

where C_2 is the configurational entropy, s_l is the internal entropy (per degree of freedom) of a mole of clusters, R_2 is the molar entropy of molecular rotation, and I_2 is the intramolecular contribution to the entropy. The rotational modes of clusters related to R_2 (cluster) are nearly equivalent to a mode of intra-cluster vibration at the limit of a long wavelength and may, therefore, be approximated by additional degrees for intra-cluster modes:

$$S_2^{\mathrm{L}} = \frac{1}{n}(T_2+C_2)_{\mathrm{cluster}} + \frac{1}{n}(3n-3)s_l + R_2^{\mathrm{L}} + I_2 \tag{7}$$

The entropy of vaporization at the triple point is given by

$$\Delta S_2^{\mathrm{L}\to\mathrm{G}} = (T_2^{\mathrm{G}}+R_2^{\mathrm{G}}) - \frac{1}{n}(T_2+C_2)_{\mathrm{cluster}} - \frac{1}{n}(3n-3)s_l - R_2^{\mathrm{L}} \tag{8}$$

The corresponding expression for an inert gas is

$$\Delta S_1^{\mathrm{L}\to\mathrm{G}} = T_1^{\mathrm{G}} - (T_1^{\mathrm{L}}+C_1^{\mathrm{L}}) \tag{9}$$

Now, if we adopt the free volume model for the liquid,

$$T_1^{\mathrm{L}}+C_1^{\mathrm{L}} = R\left(-\ln N + \frac{5}{2} + \ln N\omega_1 + \frac{3}{2}\ln(2\pi mk/h^2) + \frac{3}{2}\ln t_1\right) \tag{10}$$

and

$$\frac{1}{n}(T_2+C_2) = \frac{R}{n}\left\{-\ln(N/n) + \frac{5}{2} + \ln(N\omega_2/n) + \frac{3}{2}\ln(2\pi mnk/h^2) + \frac{3}{2}\ln t_2\right\} \tag{11}$$

where a hypothetical inert gas was chosen so that it would have the same molecular mass, m, as carbon tetrachloride. The triple point, t_1, is also a hypothetical temperature for this value of m and was determined from a plot of the triple point temperature vs. the molecular weight. In the absence of a better alternative, an assumption, $n\omega_1=\omega_2$, was made concerning the free volumes, ω_1 and ω_2. Cancelling common terms between Eq. 10 and Eq. 11, we obtain, from Eqs. 8 and 9:

$$\Delta S_2^{\mathrm{L}\to\mathrm{G}} = (T_2^{\mathrm{G}}+R_2^{\mathrm{G}}) - \frac{1}{n}\left[(T_1^{\mathrm{G}} - \Delta S_1^{\mathrm{L}\to\mathrm{G}}) - \frac{3R}{2}\ln t_1 + \frac{3R}{2}\ln t_2 + \frac{5R}{2}\ln n\right] - \frac{1}{n}(3n-3)s_l - R_2^{\mathrm{L}} \tag{12}$$

23) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," Princeton University Press (1941), Chapter IV.

24) E. R. Andrew, "Nuclear Magnetic Resonance," Cambridge University Press (1955), p. 167.

The intra-cluster entropy, s_l, may be approximated by the translational lattice entropy of solid T_2^S:

$$3s_l = T_2^S = T_2^G + R_2^G - R_2^S - \Delta S_2^{S\to G} \quad (13)$$

Finally, the estimation of R_2^L was made comparing the potential barriers hindering molecular rotation in a liquid with that in a solid at the triple point. The difference in the potential barrier arises from the difference in the average intermolecular distances (6.0 Å in liquid and 5.897 Å in solid). A good approximation to that part of intermolecular interaction which depends on the relative spatial orientation of molecules would be to use an effective cube octupole to represent a carbon tetrachloride molecule, thus taking into account the electric charge distribution and, to some extent, the shape of the molecule or the steric effect, because molecular dipole and quadrupole moments vanish by virtue of the tetrahedral symmetry of the molecules. The dispersion energy also depends on the relative molecular orientation and, therefore, contributes to the potential barrier; however, we shall incorporate the non-spherical part of the dispersion interaction into the effective octupole moment. Such interaction leads to the relation:

$$V_0(\text{liquid})/V_0(\text{solid}) = \{r(\text{solid})/r(\text{liquid})\}^7 \quad (14)$$

and the hindering potential barrier in liquid carbon tetrachloride at the triple point is found to be 2.1 kcal./mol. This value of V_0 gives R_2^L through the help of Pitzer's table.

The substitution of numerical values ($t_1 = 180°K$, $T_2^G = 40.13$ e.u., $R_2^G = 23.09$ e.u., $R_2^L = 19.42$ e.u., the other values have been taken from Tables I and II) into Eq. 12 gives, for the calculated entropy of vaporization of carbon tetrachloride at its triple point, t_2:

$$\Delta S_2^{L\to G} = 25.25 \text{ e.u.}$$

if one assesses on n the number 13, the number of nearest neighbor molecules in addition to the one at the center. This value, 25.25 e.u., is in excellent agreement with the observed value, 24.52 e.u.

Discussion

It has been suggested in the preceding sections that the small entropies of fusion of CX_4 molecules are the consequences of two effects combined; i. e. in the solid state the molecules are in the state of hindered rotation, and thus they possess a smaller degree of disorder than in an average inert gas solid, while in the liquid state they have still smaller degree of disorder than inert gas liquids. Thus, Fig. 1c shows what the actual situation looks like: both solid and liquid levels of CX_4 are lower than the corresponding levels of an inert gas in such a manner that the separation between the solid and liquid levels of CX_4 is smaller than that for inert gas. The interpretation that has been put forward in the present paper is based on the use of inert gases as the reference substance with which to compare tetrahedral molecules in regard to their behavior in condensed phases. Such a method of comparison is particularly useful because some of the properties of condensed phases are difficult to calculate from first principles. Thus, a straightforward calculation of the thermodynamic properties of liquids in terms of molecular distribution functions is a formidable task except for monatomic liquids. Also, the configurational entropy of a liquid can be estimated only to a certain limit, even in model theories. In the present treatment, such terms have been crossed out by similar terms for inert gases, and this is considered to be a major reason for the good agreement between the observed and calculated entropies of vaporization of carbon tetrachloride. Although the so-called free volume model was adopted for the liquid, the approximation imposed by the model was largely eliminated by virtue of the nature of the method of comparison. The present model of the liquid carbon tetrachloride is, of course, a statistical one. The clusters are constantly being formed and demolished. The number 13 for n should also be regarded as an average value.

One thing that has not been considered here is the effect of vacancy formation and self-diffusion in the solid at high temperatures. In the cases of argon and krypton, the measurements of heat capacity near the triple point were used to derive the equilibrium concentration of Schottky vacancies in the solid, which amounted to 2~3% at the triple points[25,26]. The contribution of the vacancy formation to the entropy would, however, be small even if there were no lattice relaxation; the difference between an inert gas and CX_4 solids would then be by far smaller. Self-diffusion in the solid will acquire an entropy of R if it is fully excited. The calculation of the entropy of diffusion in the intermediate state is not easy; here again there is a definite merit in the comparison method.

It is interesting to note that the potential barrier height hindering molecular rotation is

25) R. H. Beaumont, H. Chihara and J. A. Morrison, *Proc. Phys. Soc.*, A78, 1462 (1961).
26) A. J. E. Foreman and A. B. Lidiard, *Phil. Mag.*, 8, 97 (1963).

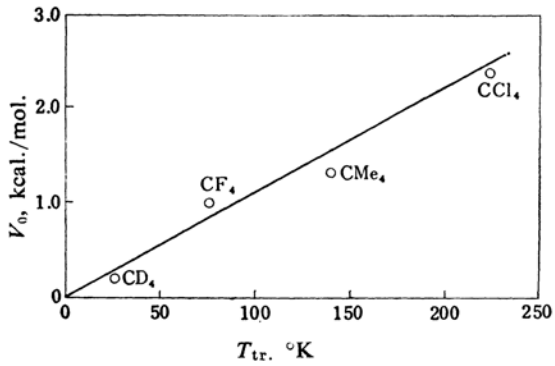

Fig. 4. Relation between the potential barrier hindering molecular rotation and the transition point.

related to the transition temperature in the solid, as is shown in Fig. 4. The point for CD_4 given by James and Keenan is also included in the figure. The points lie on a straight line which passes through the origin. While the entropy of fusion becomes larger in the order CF_4, CCl_4, CD_4 and CMe_4, the transition point becomes higher in the order CD_4, CF_4, CMe_4 and CCl_4, and so does the hindering potential. It is believed that such a linear relation between V_0 and the transition temperature justifies the treatment of a solid developed in the present paper. The apparently irregular order of the entropies of fusion has thus been straightened out.

Summary

By a comparison of the entropies of sublimation at the triple points of carbon tetrafluoride, carbon tetrachloride and neopentane with those of inert gas solids, it has been shown that these molecules are in the state of hindered rotation rather than of reorientation in the solid at the respective triple points, with heights of the potential barrier of 1.0, 2.4 and 1.3 kcal./mol. respectively. The hindering potential has been shown to be proportional to the transition temperatures of these solids.

A simple model for the structure of liquid carbon tetrachloride has been presented to account for its entropy of vaporization; the model consists in assuming nearest neighbor crystallite embryos in the liquid.

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