1101. *A Study of Defects in Plastic Crystals by means of Density Measurements.*

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The densities of the following compounds have been measured, as a function of temperature, in the so-called "plastic-crystal phase" by means of a mercury-displacement method: carbon tetrachloride, cyclohexane, t-butyl chloride, t-butyl bromide, and cyclohexanol. The accuracy was about one part in 2000. Check measurements have been made on benzene, which is not a plastic crystal. The observed densities agree with those corresponding to the lattice parameters found by X-ray-diffraction studies within the limits of accuracy of the latter. Consequently, any defects in the plastic crystals studied are either Frenkel, and not Schottky, defects, or they are Schottky defects the concentration of which does not exceed about 2%, or it may be that such crystals do develop Schottky defects in excess of 2%, but that this is accompanied by a relaxation effect which reduces the increment in the molar volume per defect as their number increases.

The results for carbon tetrachloride enable an estimate to be made of the molar volume of the supercooled plastic phase at 0°K, which is not consistent with the intermolecular energy parameters obtained from studies on the vapour. A few measurements have been made of the vapour pressure of carbon tetrachloride in the plastic-crystal phase.

Among the characteristics of so-called "plastic crystals" are low entropies of fusion, softness, and plasticity. In some at least of such crystals, the molecules have unusual freedom of movement, both to reorientate themselves and to migrate within the lattice. It has been suggested that the plasticity and the molecular freedom of movement are due to a relatively high proportion of defects.[1] Although the chemical nature of a plastic crystal limits the ways in which the concentration of defects can be measured, for Schottky-type defects the concentration can in principle be determined by measuring the actual density of the crystal and comparing it with that calculated from the unit-cell dimensions. If Schottky defects are present, the observed density should be less than the calculated density. There is, however,

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[1] W. J. Dunning, *J. Phys. and Chem. Solids*, 1961, **18**, 21.

a limit, of the order of 1%, to the concentration of such defects which one can hope to detect in this way, since, by virtue of their relatively high degree of disorder, plastic crystals give poor *X*-ray-diffraction patterns. The number of usable reflections is small, and those that are observed are rather diffuse. Consequently, the cell dimensions of a plastic crystal are seldom given to better than a few hundredths of an Angstrom, corresponding to an uncertainty of 1—2% in the calculated density. Nevertheless, we have thought it worth while to make density measurements on a number of plastic crystals which have already been examined by *X*-ray crystallography.

EXPERIMENTAL

The melting points of plastic crystals cover a wide range (*e.g.*, methane 91°K, pentaerythritol 539°K), but most of the *X*-ray work has so far been carried out on crystals which melt near or below room temperature. A general method of obtaining the density of such a solid is to maintain a vessel of known internal volume, containing a known mass of the crystal, at a suitable constant temperature, and to determine the unoccupied volume by admitting a known number of moles of a near-perfect gas and measuring the resultant pressure. We spent some time developing such a method and obtained results for carbon tetrachloride in fair agreement with those given by a mercury-displacement method. However, not uncommonly, a substance in the plastic-crystal phase has a considerable vapour pressure, and appreciable errors can arise from a non-uniform distribution of the vapour in the manometric system and in the tubes connecting this with the vessel containing the crystal. These difficulties could probably be overcome, for example, by using a differential type of manometer of small dead-space (*e.g.*, a diaphragm gauge) maintained in the same thermostat as the crystal itself. We preferred, however, to use a simple dilatometric technique with mercury as the confining fluid, even though this meant that the lower temperature-limit of our measurements was then the f. p. of mercury, which restricted the choice of substances we could study. We have made measurements on carbon tetrachloride, cyclohexane, cyclohexanol, t-butyl chloride, and t-butyl bromide, and, as a check on our technique, on solid benzene, which is not a plastic crystal and for which the lattice parameters are accurately known.

A known mass of the crystal was trapped over mercury in a dilatometer of known volume. It was, of course, essential that no appreciable quantities of dissolved gas should be liberated on the solidification of the substance under examination, and the sample was therefore thoroughly degassed. As a precaution, however, the density of the solid was determined as a function of temperature not only under a pressure of *ca.* 1 atm., but also under a pressure of *ca.* 5 atm. The effect on the apparent volume of the crystal caused by the five-fold increase in pressure was always so small that it could be attributed to the actual compression of the sample and not to the compression of gas liberated on crystallization. If there had been any evidence of the presence of significant amounts of gas, further series of measurements would have been made at 10 and 15 atm., from which a correction could have been applied for the gas present.

The dilatometer had a capacity of *ca.* 20 ml., and was similar to the piezometer used by McKinney, Skinner, and Staveley,[2] except that a series of nine calibrated bulbs was incorporated in the capillary stem. The six nearest the bulb of the dilatometer had volumes of between 0·04 and 0·06 ml. and were used to measure the expansion of the solid, while the remaining three (nearest the outlet of the dilatometer) had volumes of *ca.* 0·4 ml. each and served primarily to measure the volume change on melting. The wall-thickness of the dilatometer was sufficient to withstand an internal pressure of 30 atm. The volume of the dilatometer was determined by evacuating it and filling it with mercury at 0°C to one of the calibration marks. By measuring the apparent expansion of the mercury over a range of 50°C, a mean figure for the change of the internal volume of the bulb with temperature was obtained.

All the substances studied, except cyclohexanol, were introduced into the dilatometer in the following way. The dilatometer was inverted, and joined by a cone and socket to a system of mercury cut-offs which connected it with a reservoir containing the liquid substance, a reservoir of mercury, and a mercury vapour pump. The liquid was degassed in its reservoir by freezing and pumping, and then melting and refluxing it. This series of operations was carried out four times in all. A suitable quantity of the liquid was then condensed into the dilatometer bulb which was maintained at a temperature just above the m. p. of the liquid. (The space between the main bulb of the dilatometer and the capillary bearing the calibrated bulbs was large enough

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[2] W. P. McKinney, G. F. Skinner, and L. A. K. Staveley, *J.*, 1959, 2415.

to enable a Dewar vessel to be put round the main bulb when the dilatometer was inverted.) The liquid was then frozen, the solid cooled to a temperature well below its m. p. but above the mercury m. p., and the space above the solid pumped on. Mercury was admitted to fill the dilatometer completely, which was then detached and at once turned upside down so that the solid in the bulb was above the mercury. The crystals were allowed to melt, and then very slowly refrozen. If this was done carefully, the resultant plastic crystal resembled a block of glass without any visible cracks. The dilatometer was then placed in the thermostat at a temperature just above the freezing-point of mercury, and the amount of mercury in the dilatometer adjusted so that its meniscus was at or near the lowest calibration mark.

Owing to its comparative involatility, cyclohexanol was introduced into the dilatometer bulb as liquid, and degassed in the bulb by repeating freezing and pumping. Thereafter, the procedure followed was the same as that for the other liquids, except that after the cyclohexanol had been formed in the plastic phase, it was never cooled below −10°c, since, at this temperature, it undergoes a transition with a large entropy change.

The thermostat was similar to that used by Marshall, Staveley, and Hart,[3] and its temperature was measured with the same platinum resistance thermometer. However, as thermal equilibrium between the dilatometer and the bath was quickly established, the constancy of temperature for the length of time required was maintained by manual, and not by automatic, control of the electrical-energy input needed to counterbalance the cooling provided by a refrigerant in a narrow Dewar vessel immersed in the thermostat, the Dewar vessel having a low pressure of hydrogen in the space between the walls. In this way, temperatures could be maintained to ± 0·002° without difficulty.

The first run was always carried out with the surface of the mercury in the dilatometer outlet tube at atmospheric pressure. Starting at just above the f. p. of mercury, the thermostat was heated in stages, readings of the steady temperature and the position of the mercury meniscus being taken when this meniscus was at or near a calibration mark. When the temperature had reached within two or three degrees of the m. p. of the plastic crystal, the thermostat was cooled to approximately the starting temperature of the run, and a pressure of nitrogen of *ca.* 5 atm. was applied to the contents of the dilatometer, using the fitting previously described.[2] The run was then repeated. Finally, the thermostat was heated to such a temperature, above the m. p. of the plastic crystal, that the mercury was at or near one of the upper calibration marks. Usually, one or more of the larger calibrated bulbs remained unfilled, and further measurements on the liquid could therefore be carried out. Finally the dilatometer was removed from the thermostat and weighed, giving the total weight of the mercury and substance. From this, and the known total volume of the mercury and liquid substance at a known temperature, the separate weights of mercury and substance were evaluated, since for all the liquids studied there were reliable data on the densities of the liquids as a function of temperature. It was then a straightforward matter to evaluate the molar volumes of the plastic crystals as a function of temperature.

Since plastic crystals have low entropies of fusion, impurities could produce marked pre-melting effects, and careful attention was paid to purification. That none of the substances studied showed any obvious signs of pre-melting, implied that an adequate degree of purity was achieved. The purest carbon tetrachloride available was fractionated in a forty-six-plate column. Cyclohexane was first treated with nitrating mixture, washed with dilute sodium carbonate solution, and distilled. It was then subjected to fractional freezing, half of the material being rejected, and finally fractionated. The sample used melted at 6·50°c, corresponding to a liquid-soluble/solid-insoluble impurity content of 0·06 mole %, and a chromatogram showed no sign of benzene or methylcyclopentane, the most likely impurities. Benzene was purified by means of the nickel cyanide–ammonia–benzene clathrate,[4] which gave a sample of m. p. 5·53°c. Cyclohexanol was refluxed over lime and fractionated, and the middle fraction then fractionally crystallized three times. A little sodium was added to the residue, and it was once more fractionated. The sample used had m. p. 25·13° and b. p. 161·15°c at 1 atm. t-Butyl chloride was dried and fractionated, and the fraction boiling between 50·3 and 50·5°c was fractionally crystallized six times. The final product was dried over calcium chloride and distilled, with a b. p. at 1 atm. of 50·4°c. t-Butyl bromide was dried over anhydrous magnesium sulphate in an all-glass column. The fraction boiling between 72·7 and 73·0°c was fractionally crystallized four times, and finally distilled from magnesium sulphate; it had b. p. 72·8—73·0°c at 1 atm.

[3] J. G. Marshall, L. A. K. Staveley, and K. R. Hart, *Trans. Faraday Soc.*, 1956, **52**, 19.
[4] R. F. Evans, O. Ormrod, B. B. Goalby, and L. A. K. Staveley, *J.*, 1950, 3346.

t-Butyl chloride and bromide both react with mercury, the bromide quite rapidly. The experiments with these substances were therefore carried out as quickly as possible, and, aided by the fact that for much of the time the halides were present as solids and the temperature was low, the experiments were successfully completed before any significant amount of reaction had occurred.

In the experiments on carbon tetrachloride by the gas-displacement method, helium was used. The density of the low-temperature non-plastic form was determined at three temperatures, at the two lower of which solid carbon dioxide and liquid oxygen surrounded the bulb containing the carbon tetrachloride. In the plastic-crystal region, allowance had to be made for the vapour of the crystal itself, and so measurements were made of the vapour pressure of solid carbon tetrachloride between −44°c and the m. p.

RESULTS

The results given in Table 1 refer to the solid under atmospheric pressure. The values of V_m, the molar volume in ml., should be accurate to 0·05 ml. but they are given to three decimal places as the precision is considerably greater. The expressions given for V_m as a function of the absolute temperature, T, apply to the plastic phase over the temperature range covered by the measurements. They were evaluated on a least-squares basis, using a computer.

The only substance for which measurements were made below the transition temperature was carbon tetrachloride. Since this low-temperature form appears to persist to 0°K, an expression

TABLE 1.

Experimental values of V_m, the molar volume of the solid in ml., at 1 atm. pressure at an absolute temperature T (0°c = 273·15°K).

Carbon tetrachloride

T	90·11	194·49	224·60	234·52	235·67	237·22	239·97
V_m	76·387	79·804	81·829	86·581	86·605	86·751	86·928
T	240·31	243·50	247·10	249·97			
V_m	86·932	87·132	87·414	87·668			

$$V_m = 86{\cdot}600 + 5{\cdot}723 \times 10^{-2}(T-235) + 9{\cdot}01 \times 10^{-4}(T-235)^2.$$

Cyclohexane

T	236·83	240·885	245·395	250·61	252·28	257·64	258·74
V_m	98·133	98·408	98·723	98·989	99·184	99·542	99·659
T	264·01	268·38	269·35	272·22	278·005	278·370	
V_m	100·030	100·328	100·381	100·526	100·978	100·996	

$$V_m = 81{\cdot}692 + 6{\cdot}9343 \times 10^{-2}T.$$

t-Butyl chloride

T	235·31	238·33	240·97	243·63	247·49
V_m	97·869	98·090	98·293	98·440	98·758

$$V_m = 80{\cdot}944 + 7{\cdot}1930 \times 10^{-2}T.$$

t-Butyl bromide

T	241·39	242·52	246·86	249·77	252·46
V_m	102·107	102·245	102·516	102·811	102·961

$$V_m = 83{\cdot}583 + 7{\cdot}6824 \times 10^{-2}T.$$

Cyclohexanol

T	262·685	268·45	272·61	277·56	284·12	289·34
V_m	101·547	101·820	102·022	102·221	102·572	102·945

$$V_m = 101{\cdot}465 + 3{\cdot}596 \times 10^{-2}(T-260) + 4{\cdot}68 \times 10^{-4}(T-260)^2.$$

Benzene

T	239·87	243·43	247·54	252·59	259·44	265·085	269·94
V_m	75·046	75·194	75·370	75·575	75·891	76·193	76·479

$$V_m = 75{\cdot}061 + 3{\cdot}624 \times 10^{-2}(T-240) + 3{\cdot}63 \times 10^{-4}(T-240)^2.$$

for its volume as a function of temperature should recognize that the coefficient of expansion must become zero at 0°K. The three values of V_m below the transition fit the equation:

$$V_m = 75{\cdot}987(1+6{\cdot}122\times10^{-8}T^2+6{\cdot}513\times10^{-9}T^3),$$

but the simpler equation:

$$V_m = 76{\cdot}016(1+6{\cdot}755\times10^{-9}T^3)$$

is almost equally satisfactory, and allows the coefficient of expansion to approach zero at 0°K asymptotically, as often seems to happen.[5]

The following values were obtained for p, the vapour pressure of carbon tetrachloride in the plastic-crystal phase, in mm. of mercury:

T (°K)	229·01	237·68	243·15	246·71	249·45
p	2·03	3·94	5·76	7·30	8·80

DISCUSSION

In Table 2, we give, for the six substances studied: (1) the observed molar volume, V_m, of the crystal at the temperature at which the unit-cell dimensions were determined, evaluated by interpolation or extrapolation from the V_m–T equations of Table 1; (2) the molar volume calculated from the unit-cell dimensions, and the temperature at which these were measured; (3) the volume-increase on melting, per mole (V_m for the solid at the m. p. was evaluated from the V_m–T equation and subtracted from V_m for the liquid at the m. p., estimated from the data in Timmermans' book[10]); and (4) the molar entropy of fusion.

TABLE 2.

	(1)	(2)	(3)	(4)
CCl_4	86·79	87·4 (−35°C)[6]	4·07	2·40
C_6H_{12}	100·08	101·2 (−8°C)[7]	5·315	2·29
$(CH_3)_3CCl$	97·54	94·94 (−42·5°C)[8a]	4·61	2·0
$(CH_3)_3CBr$	101·88	101·9 (−35°C)[8b]	4·03	1·8
$C_6H_{11}OH$	102·38	103·7 (+7°C)[7]	2·43	1·37
C_6H_6	76·48	76·37 (−3°C)[9]	10·35	8·44

For significance of (1), (2), (3), and (4), see text. All volumes in ml. Values in column (4) in cal. mole^{-1} deg.$^{-1}$.

We must first consider the reliability of the molar volumes in (1) and (2). We estimate that our observed V_m values are accurate to ±0·05 ml., and the good agreement between the two V_m values for benzene is therefore reassuring. For benzene, the unit-cell dimensions have been accurately determined, probably to ±0·002Å, so that the uncertainty in the calculated V_m value is about 0·1 ml. The accuracy of the molar volumes calculated from the X-ray results for the plastic crystals is altogether less, being limited partly by an uncertainty of about ±0·05 Å in the unit-cell dimensions, and partly by uncertainty as to the temperature at which these were determined. An error of 0·05 Å in the unit-cell edge means an error of 1·7—1·8% in V_m, while, since the temperatures at which the diffraction patterns were taken are usually not known to better than ±3°, this corresponds to a further uncertainty of about 0·3% in V_m. Thus, the values in column (2) can only be regarded as accurate to *ca.* 2% at best.

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[5] G. N. Lewis and M. Randall, "Thermodynamics," 2nd edn, revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, 1961, p. 131.

[6] B. Post, *Acta Cryst.*, 1959, **12**, 349.

[7] O. Hassel and A. M. Sommerfeldt, *Z. phys. Chem.*, 1938, *B***40**, 391.

[8] (*a*) B. Post, personal communication; (*b*) R. S. Schwartz, B. Post, and I. Fankuchen, *J. Amer. Chem. Soc.*, 1951, **73**, 4490.

[9] E. G. Cox and J. A. S. Smith, *Nature*, 1954, **173**, 75.

[10] J. Timmermans, "Physico-chemical constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

For cyclohexane, values of the unit-cell edge have been reported at *ca.* −78, −40, −8, and −5°c. The figures given by Hassel and Sommerfeldt[8] for −40 and −8°c are the same (8·76 Å). We have made the comparison, in Table 2, at −8°, since a value of 8·76 Å is reasonably consistent with that of 8·80 Å given by Krishna Murti[11] for −5°c. The actual and calculated molar volumes agree within 2%; certainly, the former does not appear to exceed the latter. A value of 8·41 ± 0·02 Å was given by Hassel and Kringstad[12] for a sample cooled with solid carbon dioxide–acetone, corresponding to $V_m = 90{\cdot}2$ ml. Assuming this temperature to be about −78°c, an extrapolation of our V_m–T equation would give an actual V_m value of *ca.* 95·3 ml. While the difference between the two values is now in the direction which Schottky defects demand, if it is really due to such defects it should increase with rising temperature, especially as Hassel and Sommerfeldt reported a marked increase in the diffuse nature of the diffraction pattern between −40° and −8°c, implying a considerable increase in the disorder in the crystal.

Some years ago, Post and his co-workers[8b] published a value for the unit-cell parameter of t-butyl chloride at −45°c which corresponded to a molar volume *ca.* 8% less than that estimated from our density measurements. Such a large difference would have seemed significant, but a recent redetermination[8a] of the lattice constant of this substance gave values from 8·55 to 8·6 Å for the temperature range −40° to −45°c. The V_m value corresponding to these results is given in Table 2, and it will be seen that the difference between it and the experimental figure now scarcely exceeds the experimental error.

For the compounds listed in Table 1, therefore, the only possible conclusions seem to be (i) the defects in the plastic crystals are Frenkel, and not Schottky, defects, (ii) they are Schottky defects, but their concentration does not exceed 2%, or (iii) the defects may be Schottky defects and may exceed 2%, but, as they increase in concentration, there is a relaxation effect, and the actual increment in V_m per defect gets less. The third possibility cannot be overlooked. Thus, for argon, Beaumont *et al.*,[13] from an analysis of heat capacity and expansivity data, concluded that solid argon, near its m. p., contains an appreciable proportion of Schottky vacancies, but that "the relaxation of surrounding atoms into a vacancy is probably large, so that the effective volume of a vacancy is only perhaps a quarter of the atomic volume." It is perhaps surprising that, for two of the substances studied, cyclohexanol and t-butyl chloride, the relation between V_m and T is linear almost to the m. p. This might be regarded either as evidence that the proportion of Schottky defects in these two crystals is always relatively small, or else as support for the relaxation possibility. It is interesting that, if the V_m–T equations of Table 1 are regarded as being valid to the m. p., then the calculated values, at the m. p.s, of the coefficient of expansion, $\alpha = 1/V(\partial V/\partial T)_P$, show a remarkable uniformity, the values of $10^4\,\alpha$ being as follows: carbon tetrachloride and cyclohexane, 6·85; t-butyl chloride, 7·3; t-butyl bromide, 7·4; cyclohexanol, 7·0; benzene, 7·5.

Pople and Karasz[14] have advanced an interesting order-disorder treatment of melting, which predicts that the relative volume-change on melting should increase with the entropy of fusion. This is roughly the case for the results in Table 1, but the relative volume-changes are all smaller than those which would be expected from the entropy changes, on this theory.

The results for carbon tetrachloride lead to a percentage volume increase of 5·2 at the transition. There is a close correspondence between some of the thermodynamic properties of carbon tetrachloride and carbon tetrabromide, but the volume increase at the transition in the tetrabromide is somewhat larger (*ca.* 7·1%).

Finally, carbon tetrachloride is one of the few polyatomic compounds for which intermolecular energy parameters have been evaluated. Properties of the compound as a crystal (preferably extrapolated to 0°K) can be used to test values of these parameters derived from properties of the vapour or gas. For this purpose, the crystal of carbon tetrachloride would

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[11] G. S. R. Krishna Murti, *Indian J. Phys.*, 1958, **32**, 460.

[12] O. Hassel and A. Kringstad, *Tidsskr. Kjemi og Bergvesen*, 1930, **10**, 128.

[13] R. H. Beaumont, H. Chihara, and J. A. Morrison, *Proc. Phys. Soc.*, 1961, **78**, 1462.

[14] J. A. Pople and F. E. Karasz, *J. Phys. and Chem. Solids*, 1961, **18**, 28; **20**, 294.

have to be the plastic crystal with its cubic lattice, rather than the less-symmetrical low-temperature form. The ratio of the volume of carbon tetrachloride in its low-temperature form at the transition temperature to that at 0°K is 1·076. If we suppose that the same ratio would hold for the supercooled plastic crystal (which cannot be far wrong, as the coefficient of expansion would still have to become zero at 0°K), the estimate of V_m for the plastic phase at 0°K would be 80·0 ml., corresponding to a distance of 5·73 Å between nearest neighbours in the lattice. This is less than the figure of 5·881 Å given by Hirschfelder *et al.*[15] (from an analysis of vapour-viscosity data) for the distance at which the intermolecular energy of a pair of carbon tetrachloride molecules is zero. Acceptance of the latter figure would mean that, at a distance of 5·73 Å, a molecule in the lattice would be in a state of net repulsion with respect to its nearest neighbours, which illustrates the unreliability of applying intermolecular energy parameters, deduced from properties of a polyatomic compound as a gas, to problems relating to the same compound in its condensed states.

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[15] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley New York, 1954, p. 1111.