

SOLID TRANSITIONS IN MIXED CRYSTALS OF ETHYLENE DICHLORIDE AND ETHYLENE DIBROMIDE

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INTRODUCTION

In principle, the heat capacity curve of a solid substance can give information about the dependence of energy absorption on temperature of the crystal lattice, and hence on the mechanism of any phase changes which occur therein. In practice, however, the amount of information is limited (a) by the fact that a considerable contribution to the measured C_p comes from the term $\beta^2 VT/\alpha$; (b) by the lack of an adequate theory of the heat capacities of complex crystals. In certain cases, though, considerable insight can be obtained by diluting the lattice of a compound which undergoes a phase transition with a second kind of molecule or ion, and observing the effect on the nature and magnitude of the transition. The added component has usually been one which itself has no transitions¹, but a few studies have been made of mixed crystals both of whose components exhibit solid transitions², when the phenomena are naturally more complex.

This paper concerns heat capacity measurements on mixtures of ethylene dichloride and dibromide, both of which undergo solid transitions, and form a continuous series of mixed crystals.

EXPERIMENTAL

The experimental method will be fully described elsewhere³. The calorimeter assembly was closely similar to that of Aston and Ziemer⁴. The calorimeter vessel, of about 70 cm³ capacity, was freely suspended inside a copper "mantle", itself suspended from a lead block inside an evacuated space. A re-entrant well in the calorimeter held a hollow former carrying a heating coil, inside which was a platinum resistance thermometer. The latter consisted of two strain-free spirals of 48 S.W.G. platinum wire, supported inside a platinum capsule. The thermometer was calibrated at the ice point and the boiling points of naphthalene, water and liquid oxygen. A double potentiometer of the type described by White was used for all the electrical measurements. The standard procedure for the measurement of heat capacities was followed. Determination of known thermal quantities showed that the absolute accuracy of the results was at least ± 0.5 per cent; the internal consistency was considerably better—about ± 0.1 per cent.

Ethylene dibromide and dichloride were carefully purified, finally by distillation from a 120 cm column packed with Fenske helices. The refractive index of the final sample of the dibromide agreed exactly with the value

quoted by Timmermanns⁵, while the melting range of the dichloride showed it to contain only 0.03 mole per cent of liquid-soluble, solid-insoluble impurity. The samples were kept out of contact with moisture, and the filling of the calorimeter vessel was carried out in a dry-box.

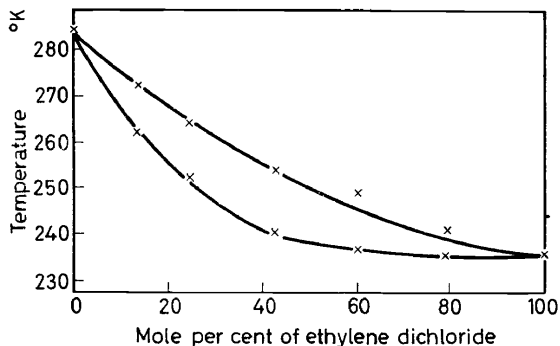


Figure 1. Freezing and melting curves for ethylene dichloride-ethylene dibromide mixtures

The phase diagram for the ethylene dichloride-ethylene dibromide system⁶ (Figure 1) shows that these compounds give a complete series of mixed crystals just below the melting curve. The liquid mixtures were frozen as rapidly as possible, in order to minimize phase separation on cooling, although to some extent this was obviously inevitable, and normally a mixture was not allowed to melt again until all measurements on it had been made. But in a few cases measurements were made on the same mixture before melting, and after melting and re-freezing, and the results were found to agree, provided the mixture had been annealed after each freezing, by the following method. The frozen mixture was cooled as rapidly as possible to well below the temperature of the lowest transition for the system, and was then heated to within a few degrees of its melting temperature, held there for some hours, and then cooled very slowly to below the temperature of the lowest transition. When a mixture had been taken three times through this heating and cooling cycle, it was possible to obtain a completely reproducible specific heat curve for the whole temperature range. For any mixture, as much as possible of the transition region was always covered by continuous working.

RESULTS

For any mixture at any temperature, the heat capacity quoted is the total heat capacity of the contents of the calorimeter, divided by the total number of gram-molecules present—that is, it is a mean molar heat capacity.

Figures 2 and 11 give the heat capacity curves for pure ethylene dibromide and dichloride⁷, while Figures 3-10 show the curves for the eight mixtures investigated. These contained respectively 3, 8, 18, 43.5, 51, 60, 80 and 90 mole per cent of ethylene dichloride. For the discussion of the results, four regions of interest may be distinguished.

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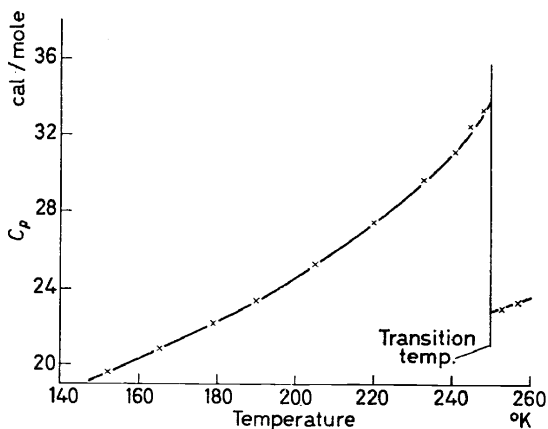


Figure 2. Heat capacity curve for ethylene dibromide

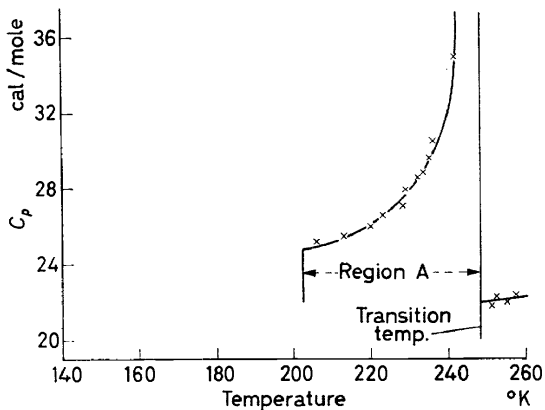


Figure 3. 3 mole per cent of ethylene dichloride

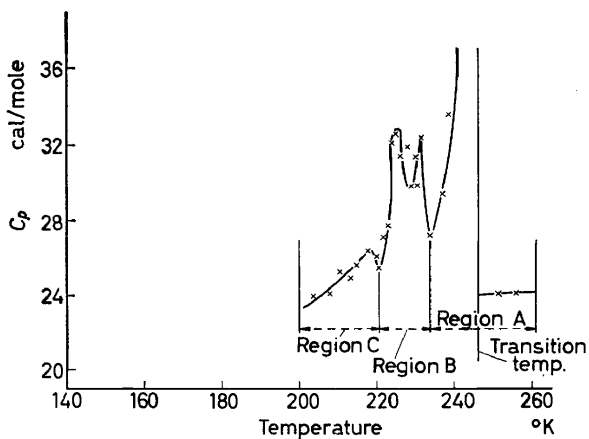


Figure 4. 8 mole per cent of ethylene dichloride

A. *Around 250°K*—Ethylene dibromide undergoes a sharp transition at 250°K which also appears (though at slightly lower temperatures) for the mixtures containing 8 and 18 mole per cent of dichloride.

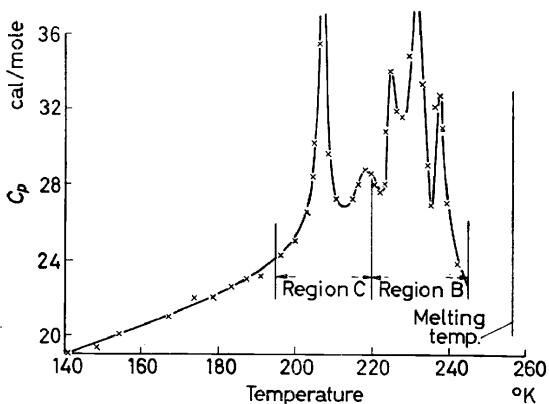


Figure 5. 18 mole per cent of ethylene dichloride

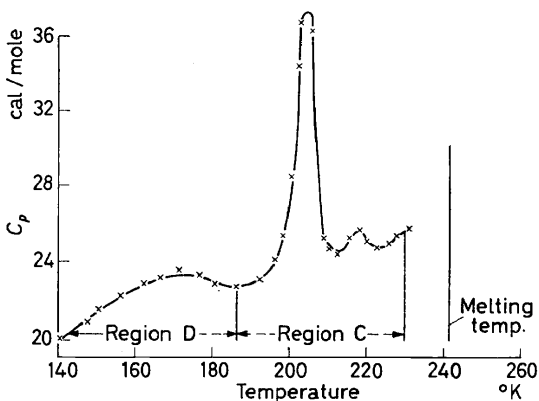


Figure 6. 43.5 mole per cent of ethylene dichloride

B. *The range 225–235°K*—For mixtures with 8 and 18 mole per cent of dichloride, this is a region of complexity, with two or three maxima in this part of the heat capacity curve.

C. *The range 205–215°K*—Mixtures containing from 18 to 60 mole per cent of ethylene dichloride have a marked, narrow maximum heat capacity at about 206°K, with a much smaller subsidiary peak about 10° higher.

D. *Below 178°K*—Ethylene dichloride has a very broad hump in its heat capacity curve, with a maximum at about 178°K. On addition of dibromide the height of this hump is reduced, while its breadth is more or less unaffected. For 90 and 80 mole per cent of dichloride the hump is as sharp as for the pure dichloride, while for the mixtures with from 43.5

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to 60 mole per cent of dichloride the hump is appreciably more rounded. The temperature of the maximum is first depressed by addition of dibromide, but with increasing amounts again rises slightly.

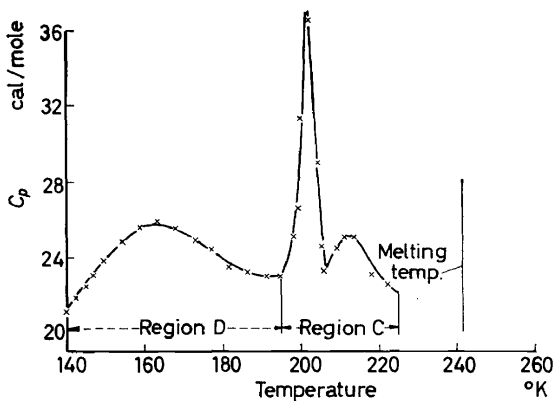


Figure 7. 51.0 mole per cent of ethylene dichloride

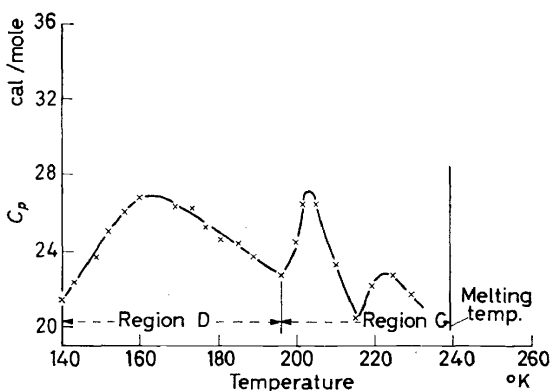


Figure 8. 60.0 mole per cent of ethylene dichloride

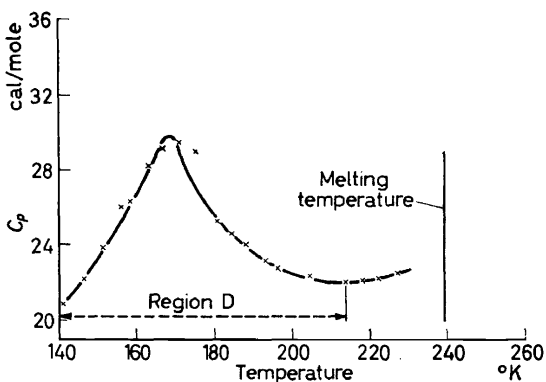


Figure 9. 80.0 mole per cent of ethylene dichloride

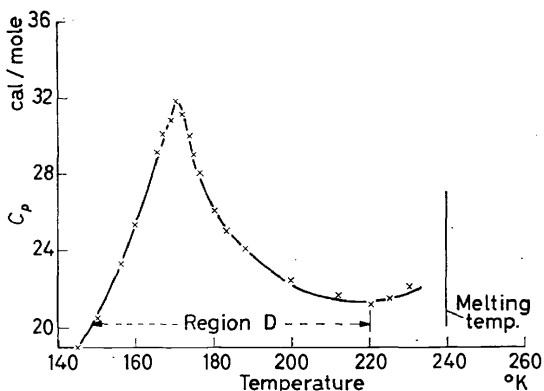


Figure 10. 90.0 mole per cent of ethylene dichloride

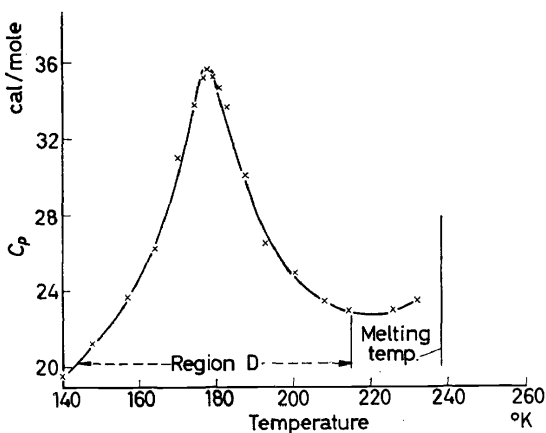


Figure 11. Heat capacity curve for ethylene dichloride

DISCUSSION

In the interpretation of these results, the following facts about ethylene dibromide and dichloride have to be borne in mind.

Ethylene dichloride crystallizes with a monoclinic space lattice containing two molecules per unit cell⁸. Infra-red absorption measurements⁹ show the molecules to be in the fully-extended or "trans" configuration, while both X-ray and proton magnetic resonance measurements^{8, 10} are consistent with the gradual transition at 178°K in the pure compound, marking the onset of free rotation of the ethylene dichloride molecules, probably about their axes of least inertia. Otherwise, the crystal structure is not affected by the transition. Ethylene dibromide has the same crystal structure as the dichloride (the β modification) above its sharp transition at 250°K, but exists in a different monoclinic form (the α modification) with four molecules to the unit cell, below this temperature¹¹. As in the

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case of the dichloride, the dibromide molecules are in the *trans* configuration and seem to be rotating as a whole above the transition point.

The sharp transition in pure ethylene dibromide is preceded by a seemingly anomalous rise in heat capacity, above the values to be expected from the curve at lower temperatures. Pitzer⁷ suggested that this rise foreshadowed a second-order rotational change, similar to that in the dichloride. Because of greater lattice forces with the dibromide, molecular rotation was more difficult, the transition was accordingly delayed to a higher temperature, and before it could be completed, it gave place to a radical reorganization of the lattice, accompanied by a first-order anomaly. However, it is doubtful whether this view can be accepted, in the light of the information on the crystal structure of ethylene dibromide, which was not available to Pitzer. What can presumably be said, is that rotation is more difficult in the α -dibromide lattice than in the β -dichloride lattice.

Timmermanns' phase-rule study showed the formation of a continuous series of mixed crystals of ethylene dichloride and dibromide just below the freezing point, which is reasonable in view of the high temperature form of the dibromide having the same crystal structure as ethylene dichloride. Timmermanns did not report phase separation on continued cooling of the mixed crystals, but this is nevertheless likely to occur. When a crystal mainly of the dibromide is cooled, it will certainly undergo a lattice change at a temperature not much different from that for the pure dibromide. At lower temperatures, then, the dichloride molecules present will be in an "alien" lattice, and there will probably be a limit to the number which can be so accommodated, which may correspond to quite a small solubility of dichloride in dibromide. On the other hand, no such lattice change will occur when a crystal consisting mainly of dichloride is cooled. The dibromide molecules in such a crystal will therefore always be in a lattice which is at any rate the equilibrium lattice for dibromide at sufficiently high temperatures. Thus, though there must also be a solubility limit for dibromide in dichloride, it should be considerably greater than in the converse case. As will appear from consideration of the heat capacity curves, these solubility limits probably correspond to about 5 mole per cent of dichloride in dibromide, and 60 mole per cent of dibromide in dichloride. Hence, mixed crystals with less than about 5 or more than about 40 mole per cent of dichloride would remain homogeneous on cooling, while crystals of compositions between these values would separate into two components, of approximately these two compositions.

A further possibility is the formation of a super-lattice. If this should happen—most probably for mixed crystals with more or less equal proportions of each component—there would probably be a Curie point at some temperature, when the ordered, low-temperature arrangement, with the nearest neighbours of one kind of molecule predominantly those of the other kind, gave way to a disordered high-temperature form, in which the nearest neighbours were themselves a random mixture of the two components.

Because of these possible complications, it is only with mixed crystals containing relatively small proportions of either component that the effect of this component on the phase transition of the main component is likely

to be clearly discernible. Such replacement of the major component will (a) change the lattice spacing; (b) modify the lattice forces. The change in lattice forces will be partly due to the attendant change in lattice spacing, and partly due to the less symmetrical force field resulting from partial replacement. In addition, the actual intermolecular forces, for a given distance, will be changed. If these forces are mainly dispersion forces, they will be greater the larger the molecules concerned. If, on the other hand, the C-halogen bond dipoles make a sizeable contribution (although, of course, the molecules as a whole are non-polar in the *trans* configuration) then replacement of dichloride by dibromide may lead to a net reduction in intermolecular forces. The effect of replacement on forces and hence on transitions, cannot therefore be clear-cut. With these preliminary remarks in mind, the results for each of the four regions distinguished can now be considered.

Region A

If ethylene dichloride were soluble in the high-temperature (β) form of the dibromide (which has the same crystal structure) but insoluble in the low-temperature (α) form, small additions of dichloride should lower the dibromide transition point according to the equation:

$$\Delta T = \frac{RT^2}{\Delta H} \cdot \frac{n_2}{n_1}$$

Use of this equation, however, would indicate a lowering of about 8° for the addition of 3 mole per cent of dichloride, as against the observed lowering of less than 2° . Thus, it seems that the dichloride (as expected) must be to some extent soluble in the low-temperature form of the dibromide, so that the free energy of both α - and β -dibromide are lowered by addition of dichloride and the above equation does not apply. The less symmetrical force field in the mixed crystal should facilitate lattice transformation, which should therefore set in at a lower temperature than in the pure compound. For the same reason, the transition may not now be strictly isothermal, and experiment actually shows it to be less sharp than in the pure dibromide.

Region D

The unusual broadness of the rotational transition at 178°K in pure ethylene dichloride presumably means that the forces opposing rotation are small, so that the first molecules to rotate can do so quite easily, and no drastic loosening of the force field inhibiting rotation of the remaining molecules is thereby caused. The dependence on composition of the temperature of the "dichloride" transition is shown in *Figure 12*. For the replacement of up to 40 mole per cent of dichloride by dibromide, the transition temperature is lowered, which indicates that the lattice forces are decreased, presumably because the reduction in dipole-dipole attractions outweighs the larger dispersion forces to be expected, when dichloride is replaced by dibromide. The rise in transition temperature for more than 40 mole per cent of dibromide is understandable in terms of super-lattice formation, as is the change in the nature of the hump in

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the heat capacity curve between the 60 and 80 mole per cent mixtures, and these topics will be discussed in the next section.

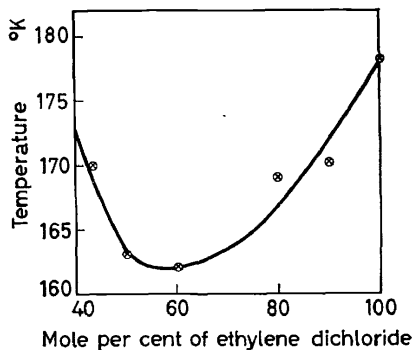


Figure 12. Variation of ethylene dichloride transition with composition

Region C

Phenomena in this temperature range differ from those discussed for the other temperature ranges, since the two interconnected peaks near 210°K occur for neither of the pure compounds. The lower peak, at about 206°K , might be due to onset of rotation of ethylene dibromide molecules, rotation having already set in for the dichloride in these mixtures. However, the shape of this peak is quite different from that occurring in the dichloride-rich mixtures, and its temperature varies very little with composition, unlike that of the dichloride peak. In addition, there is also the smaller subsidiary peak about 10° higher to be explained. For these reasons the 206° peak may more probably be associated with a super-lattice transformation. Although such a change will naturally be much more difficult for a molecular crystal than for an alloy, there seems no reason in principle why it should not also occur in this case—especially when the lattice forces have been loosened by a preliminary acquirement of rotational freedom. When there is a great disparity in the relative amounts of ethylene dichloride and dibromide, there will be little difference between an ordered and a disordered arrangement, and any super-lattice anomaly would be very slight. But with roughly equal proportions the anomaly should be more marked. It may therefore be significant that the 206° peak is found only for mixtures containing from about 40 to 60 mole per cent of dibromide, and also for the 82 per cent mixture, which is discussed in the next section. Further, the 206° peak is not dissimilar in shape to those usually found for super-lattice changes, and the small dependence of the transition temperature on composition is broadly consistent with the effect of composition on Curie point for certain alloy systems^{1,2}.

If mixed crystals with from 40 to 60 mole per cent of ethylene dichloride exist as super-lattices at low temperatures, each kind of molecule will then to a considerable extent be segregated on its own lattice and surrounded predominantly by molecules of the other kind. It may not be possible for ethylene dibromide molecules to rotate in such a situation, partly because

of their mutual isolation, making co-operative effects unlikely, and partly because dipole-dipole forces inhibiting rotation will be larger between an ethylene dibromide and an ethylene dichloride molecule than between two ethylene dibromide molecules. If de-segregation is responsible for the transition at 206°K the above factors then cease to operate, so that the smaller, higher peak may be caused by the onset of rotation for any non-rotating ethylene dibromide molecules. Its small magnitude may be due to full rotational freedom not even then being acquired, or to only a proportion of the dibromide molecules having had their rotation previously inhibited.

On this basis, mixtures with less than 40 mole per cent of dibromide will show no peak at 206°, for reasons already discussed. The dichloride peak is than as sharp as in the pure compound, and may indeed involve the rotation of dichloride and dibromide molecules alike, in the disordered crystal. From 40 to 60 mole per cent of dibromide, however, the mutual isolation of the dichloride molecules may well be responsible:

(a) For the change in character of the "dichloride" transition. It now becomes much smaller in area and more rounded in shape than for mixtures with less than 40 mole per cent of dibromide, possibly because the rotation now involves only the dichloride molecules.

(b) For the fact that the temperature of the transition now rises again, the coupling between dichloride molecules being lessened, by reason of their segregation.

Region B

The complex behaviour for mixtures with 8 and 18 mole per cent of ethylene dichloride in this region, is almost certainly due to the existence of a solid miscibility gap. As already discussed, the existence of such a gap, from about 5 to 40 mole per cent of dichloride, would result in a partial or complete separation in a cooled, annealed mixture with a gross composition falling between these limits, into an intimate aggregate of two mixed crystals, with respectively about 5 and about 40 mole per cent of dichloride. When such a mixture was heated, it would display the following features:

(a) A transition or transitions around 210°K, due to the 40 mole per cent component; this component might also show an ethylene dichloride transition at a lower temperature. In fact, the latter transition is only just apparent for the mixture with 43.5 mole per cent dichloride, so it may well be undetectable in the dichloride-rich crystal on that side of the miscibility gap, for a gross composition between the miscibility limits.

(b) One or more maxima, due to the absorption of energy on re-mixing to give a single mixed crystal.

(c) A dibromide-type transition, occurring at a temperature appropriate to the mixed crystal resulting from the re-mixing.

The critical (solid) solution temperature would probably lie not far below the melting curve for the system, so that process (a) should certainly occur before any re-mixing. Processes (b) and (c), however, might occur at about the same temperature, and the previous occurrence or non-

occurrence of re-mixing would obviously affect the temperature of process (c).

The above discussion has been in terms of complete separation and remixing, but fairly obviously this would not take place. It is considered that the annealing procedure used would produce at least a partial separation into two mixed crystals, possibly in domains of limited extent, and that there would be some degree of re-mixing across the domain boundaries on heating. In this case, the course of events would naturally be less clear-cut than that discussed above, and several maxima might appear as a result of the mixing process, instead of only one.

In fact, the mixture with 18 mole per cent dichloride does show peaks at 212° and 218°K, corresponding to those for the middle-range compositions. They are smaller than for the mixture with 44 mole per cent of dichloride, presumably because of the smaller amount of this component present, in the partially separated mixed crystal. Whether the isolated peak at 216°K for the 8 mole per cent mixture is also due to a 40 per cent component is perhaps more doubtful. On the other hand, the 8 mole per cent mixture has an unmistakable dibromide type transition at 247°K, which is not much lower than that observed for the 3 mole per cent mixture. This is quite understandable if the peak in the 8 mole per cent mixture is actually due to a 5 mole per cent component. That the 18 mole per cent mixture shows no dibromide-type peak is possibly due to the fact that the melting temperature for this composition is lower than the expected temperature of a dibromide transition, even for a 5 mole per cent crystal.

Confidence is therefore felt in attributing the broad features of the heat capacity curves for the 8 and 18 mole per cent mixtures to a partial separation into two mixed crystals, even though it is hardly possible to analyse these curves in detail.

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