579. *Solid Transitions in Mixed Crystals of Ethylene Dichloride and Ethylene Dibromide.*

By J. E. Spice, G. A. Harrow, C. R. McGowan, and E. B. Smith.

Heat capacities have been measured for eight mixed crystals of ethylene dichloride and ethylene dibromide. The solid transitions observed are discussed in terms of the transitions shown by the pure compounds, and of the lattice forces in the mixed crystals. They indicate a solid miscibility gap over the approximate range 5—40 moles % of ethylene dichloride; super-lattices may be formed at low temperatures in crystals with nearly equal proportions of the two constituents.

Heat capacities give information on the size of lattice forces in crystals, and many qualitative results which bear on the mechanism of solid transitions have been obtained from such studies. Various factors render it difficult to derive more precise information. First, a considerable contribution to the measured C_p (heat capacity at constant pressure) comes from the term β^2VT/α which, although obviously affected by the overall dynamics of the crystal, is not related as directly to the energetics of the crystal as is C_V (the heat capacity at constant volume). Secondly, little work has been done on the theory of the heat capacities of complex crystals. One or two workers [1] have separated C_p for certain compounds into the contributions arising from inter- and intra-molecular motions of various kinds, but the information necessary for this is often lacking. In an alternative approach, the effect is studied of 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 temperature and nature of the transition. The added component has usually been an inert diluent,[2] but a few studies have been made of the transitions occurring in mixed crystals both of whose components exhibit solid transitions.[3] The phenomena in such cases are naturally more complex than for simple dilution.

This paper concerns heat-capacity measurements of mixtures of ethylene dichloride and ethylene dibromide. The dibromide has a first-order transition just below its melting point, while the dichloride has a transition of higher order at a fairly low temperature.

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[1] Lawson, *Phys. Rev.*, 1940, **57**, 417; Marshall, Staveley, and Hart, *Trans. Faraday Soc.*, 1956, **52**, 19.

[2] Eucken and Veith, *Z. phys. Chem.*, 1936, *B*, **34**, 275.

[3] Bartholomé, Drikos, and Eucken, *Z. phys. Chem.*, 1938, *B*, **39**, 371; Mandleburg and Staveley, *J.*, 1950, 2736.

The two compounds form a continuous series of mixed crystals,[4] so that heat capacity measurements should throw light on the forces affecting each kind of molecule.

EXPERIMENTAL

Calorimeter and Auxiliary Apparatus.—The calorimeter assembly used for most of the measurements (calorimeter II) was closely similar to that of Aston and Ziemer.[5] The calorimeter vessel was of about 70 c.c. capacity, and was suspended inside a cylindrical copper " mantle," with conical ends, which itself hung from a lead block. This block was suspended from a circular plate to which were soldered the outer brass can and the main pumping tube, which also carried the electrical leads. During measurements the outer can and the mantle were continuously evacuated. The whole assembly was immersed either in a mixture containing solid carbon dioxide or in liquid nitrogen, according to the temperature range. The three portions of the mantle carried heating coils, by means of which its temperature could be kept equal to that of the calorimeter vessel. Copper–constantan thermocouples showed differences of temperature between the mantle and the calorimeter vessel. The coil heating the calorimeter was wound in a shallow inset in the outer face of a hollow copper cylinder, which was a push-fit in the axial well of the calorimeter vessel; it was of 44 S.W.G. constantan, and had a resistance of 120 ohms at room temperature. The platinum resistance thermometer consisted of two resistance elements, contained in a platinum capsule 7 cm. long and 6 mm. in outside diameter; [6] this fitted tightly inside the copper cylinder carrying the heating element. Each thermometer element was made by winding about 150 cm. of 48 S.W.G. " thermopure " platinum wire on a 1 mm. steel mandrel in a lathe, and then drawing it out to form a fairly close spiral, which was supported in a thin Pyrex tube, 2 mm. in outside diameter. Thicker platinum leads were soldered to the ends of the elements and brought out through a bulb of lead glass, fused to the open end of the platinum sheath. The complete thermometer was filled with helium to a pressure of 0·5 atm. at room temperature; it had a resistance of 69·3 ohms at 0°. After careful annealing, the thermometer was calibrated by measuring its resistance at the ice-point and at the b. p.s of naphthalene, water, and liquid oxygen. From these results the four constants of the International Temperature Scale were determined, and deviation graphs were plotted so as to permit the accurate calculation of temperatures from a linear function of the thermometer resistance. A double potentiometer was used for the measurement of both temperature and energy input, in the usual manner. The galvanometer sensitivity was such that with a lamp-scale distance of two m., a spot deflection of 1 cm. corresponded to a temperature change of 0·001°.

The determination of heat capacities and heats of fusion followed the standard procedure. Away from the region of a transition, thermal equilibrium was rapidly attained, but within the transition region conditions were more sluggish, and an hour might elapse between the end of a heating period and the re-attainment of a steady temperature drift. With care, the temperature of the calorimeter could be made to change by as little as 0·001° in five min., and heat-capacity determinations were usually made under these conditions.

For the earlier measurements a glass calorimeter (calorimeter I) was employed, consisting of a cylindrical Pyrex vessel of about 80 c.c. capacity, with a combined resistance thermometer–heater of 40 S.W.G. platinum wire wound directly on it. This had a resistance of ~175 ohms at room temperature. The calorimeter vessel was suspended inside a brass mantle fitted with a heating coil, and this in turn was freely suspended inside a continuously evacuated outer vessel, immersed in the cooling medium. Thermocouples showed the difference in temperature between the calorimeter and its surroundings. The electrical measurements and general experimental procedure were the same as for calorimeter II. Calorimeter I gave quite accurate results except in transition regions, where the glass calorimeter and external thermometer were ill-adapted for following sluggish transformations requiring considerable time.

Materials.—Ethylene dibromide was washed with concentrated sulphuric acid and then with dilute sodium carbonate, dried ($CaCl_2$), and kept over phosphorus pentoxide for a week. It was distilled from mercury through a 12″ Dufton column, and the fraction boiling above 130·5° was then fractionated over anhydrous sodium sulphate, through a 120 cm. column

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[4] Timmermans, *Bull. Soc. chim. belges*, 1927, **36**, 186.

[5] Aston and Ziemer, *J. Amer. Chem. Soc.*, 1946, **68**, 1405.

[6] Barber, *J. Sci. Instr.*, 1950, **27**, 47.

packed with Fenske helices and with a reflux ratio of 50 : 1. For the final sample n_D^{15} = 1·54160, agreeing with the value quoted by Timmermans.[7]

Ethylene dichloride was washed with 5% aqueous potassium hydroxide and then with water and dried ($CaCl_2$ overnight; P_2O_5 for a week), then fractionated over anhydrous sodium sulphate in the 120 cm. column at a reflux ratio of 50 : 1. The fraction of b. p. 83·5° had n_D 1·44756 (lit.,[7] 1·44759). Determination of the melting range showed the sample to contain only 0·03 mole % of liquid-soluble solid-insoluble impurity.

The purified samples were sealed in Pyrex tubes, out of contact with moisture. For further data on purity see below.

Accuracy and Reproducibility of the Measurements.—The heat capacity of the empty calorimeter II was measured over the range 80—300° K. The mean deviation of the experimental points from the best smooth curve through them was ±0·1%, which represents the inherent reproducibility of the calorimetric measurements. As regards absolute accuracy, the following Tables, showing the results obtained in the present work and those of previous workers, indicate that no large systematic errors are likely to affect the accuracy.

Heat Capacities.—Harrow, using calorimeter I, obtained values for ethylene dibromide over the temperature range 170—280° about 1% lower than those reported by Pitzer.[8] Five measurements were made by Smith (calorimeter II) on ethylene dichloride, over the range 220—250° K. The average deviation from Pitzer's values was +0·7%.

Melting Points and Transition Points.—The values obtained in the present work are compared in Table 1, with those reported previously.

Heats of Fusion and Transition.—The results are shown in Table 2.

TABLE 1. *Melting and transition points.*

	$C_2H_4Cl_2$	$C_2H_4Br_2$	
	M. p. (K)	M. p. (K)	Trans. pt. (K)
White and Morgan [a]		249·0°	282·3°
Morino [b]		248·4	
Le Blanc and Mobius [c]			283·07
Timmermans [4]	237·6°	249·1	283·10
Railing [9]	237·65	250·6	283·0
Pitzer [8]	237·2 ± 0·1	249·55 ± 0·1	283·0
Harrow (cal. I)	237·5 ± 0·2	249·6 ± 0·2	282·9 ± 0·2
McGowan (cal. II)	237·60 ± 0·05	249·65 ± 0·05	
Smith (cal. II)	237·65 ± 0·05		

[a] White and Morgan, *J. Chem. Phys.*, 1937, **5**, 655. [b] Morino, *J. Chem. Soc. Japan*, 1939, **60**, 222. [c] Le Blanc and Mobius, *Ber. Verhandl. Sachs. Akad. Wiss. Leipzig, Math. Phys. Klasse*, 1933, **85**, 75.

TABLE 2. *Heats of fusion and transition.*

Heat of fusion (cal./mole) of $C_2H_4Cl_2$		Heat of transition (cal./mole) $C_2H_4Br_2$	
Railing [9]	2090 ± 21	Pitzer [8]	463·8
Pitzer [8]	2112 ± 2	Harrow (cal. I)	460·7 ± 3
Smith (cal. II)	2106 ± 4		

From all these comparisons the results with calorimeter II appear reliable within ~0·5% (their internal consistency was considerably better). Calorimeter I was less adaptable, but its absolute accuracy was quite good. For following closely the progress of slow thermal transitions, however, calorimeter II was very much better than calorimeter I.

RESULTS

Eight mixtures were investigated, which contained severally 3, 8, 18, 43·5, 51, 60, 80, and 90 moles % of ethylene dichloride. At a given temperature, the heat capacity of the empty calorimeter was subtracted from the total heat capacity of the calorimeter and its contents, and the result was divided by the total number of moles of both components, so as to give a mean molar heat capacity.

Ethylene dichloride and dibromide form a complete series of mixed crystals (at least just

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[7] Timmermans and Martin, *J. Chim. phys.*, 1928, **25**, 411.
[8] Pitzer, *J. Amer. Chem. Soc.*, 1940, **62**, 331.
[9] Railing, *J. Amer. Chem. Soc.*, 1939, **61**, 3349.

below the melting curve) whose melting temperatures lie between the m. p. of the pure components. Since the mixtures had to be made as liquids, there was the possibility that, on cooling, phase separation might occur, to give an inhomogeneous solid consisting of mixed crystals of various compositions. The liquid mixtures were therefore frozen as rapidly as possible, and normally a mixture was not allowed to melt again until all the measurements on it had been completed. A few determinations were made on the same mixture before and after melting, and it was found that, provided the annealing procedure about to be described had been carried out, the results agreed to within the usual experimental uncertainty. Until the importance of careful annealing was realised, extremely erratic results were obtained. It was impossible to reproduce transition temperatures to within closer limits than ~1° and small transitions sometimes appeared. In investigating solid transitions it is always necessary to guard against supercooling, and for the present system—where, as will be seen, phenomena are more complex than usual—this was particularly important. The following cooling and annealing procedure was found satisfactory. Each liquid mixture was cooled as rapidly as possible, by admitting hydrogen to the outer calorimeter spaces and bringing a large vessel of liquid nitrogen suddenly around the calorimeter can, to well below the temperature of the lowest transition for that mixture. It was then heated to within a few degrees of its melting temperature and held there for some hours. The calorimeter was next cooled very slowly to below the lowest transition. After the calorimeter and contents had been taken through this heating and cooling cycle three times, reproducible specific-heat curves were obtained over the region of any transition. With a properly annealed crystal the same heat capacity points could be obtained after the mixture had been taken through a transition and then cooled below it again, or after melting the mixture and then freezing and annealing it again. Nevertheless, as much as possible of any transition region was always covered by continuous working.

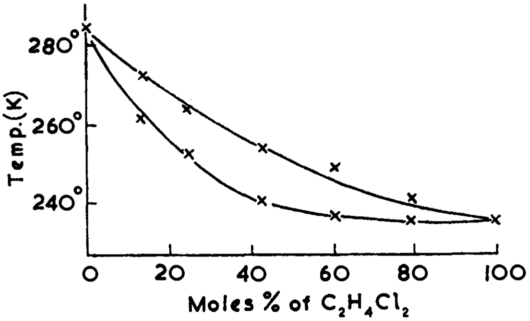


FIG. 1. *Freezing and melting diagram of mixtures of ethylene dichloride and dibromide.*

Fig. 1 is the phase diagram for ethylene dichloride–ethylene dibromide, as obtained by Timmermans;[4] Figs. 2—11 show the variation of the mean molar heat capacity C_p with the absolute temperature, for the pure compounds[8] and for the eight mixtures. All the results shown for mixed crystals were obtained with calorimeter II, except that for 90% ethylene dichloride. The 3% mixture was investigated also in calorimeter I, the curve obtained being virtually identical with that shown. The remaining results from calorimeter I were later confirmed with calorimeter II as regards the temperatures of transitions, but more detail was revealed. Such remaining mixtures were in the intermediate region (10—60 moles % of ethylene dichloride), and calorimeter I possessed insufficient " resolving power " to reveal the full complexity of the heat capacity curves for such compositions. On each curve the melting temperature for that mixture is indicated.

For the discussion of these results, it is convenient to distinguish four temperature ranges:

(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 3, 8, and 18 moles % of ethylene dichloride.

(B) 225—235° K. For the mixtures with 8 and 18 moles % of dichloride, this is a region of complexity, with two or three maxima in the heat capacity curve.

(C) 205—218° K. Mixtures containing 18—60 moles % of ethylene dichloride have a marked, narrow, maximum heat capacity at ~206° K, with a much smaller subsidiary peak ~10° higher.

(D) *Below* 178° K. Ethylene dichloride has a very broad hump in its heat capacity curve, with a maximum at ~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 moles % of dichloride the hump is as sharp as for the pure dichloride; for the mixtures with 43·5—60 moles % of dichloride, it is appreciably more rounded. The temperature of the maximum is first depressed by addition of dibromide, but with increasing amounts again rises slightly.

FIGS. 2—11. *Heat-capacity curves.* TP = *Transition temperature,* MP = *melting temperature. For* A, B, C, D *see text.*

FIG. 2: Pure $C_2H_4Br_2$.

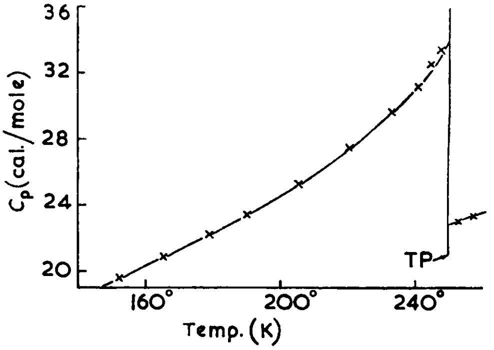


FIG. 3: 3 Moles % of $C_2H_4Cl_2$.

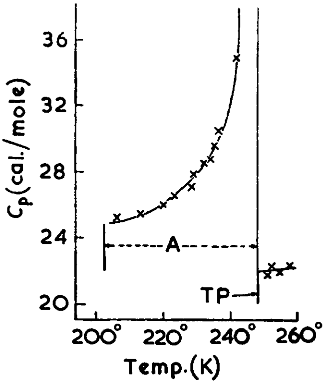


FIG. 4: 8 Moles % of $C_2H_4Cl_2$.

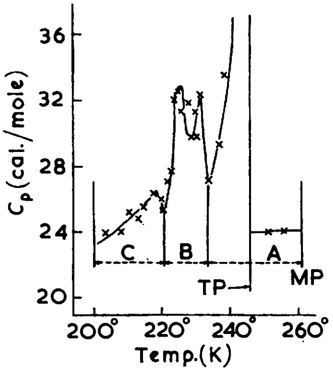


FIG. 5: 18 Moles % of $C_2H_4Cl_2$.

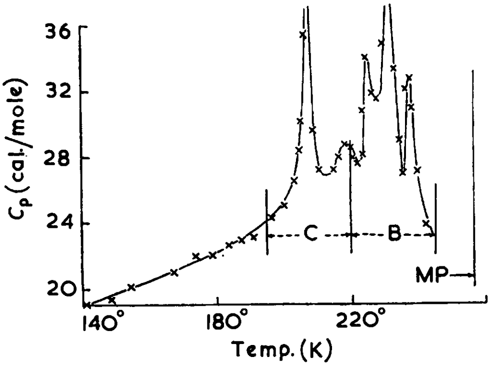


FIG. 6: 43·5 Moles % of $C_2H_4Cl_2$.

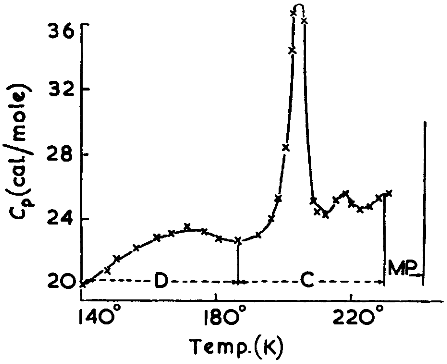


FIG. 7: 51·0 Moles % of $C_2H_4Cl_2$.

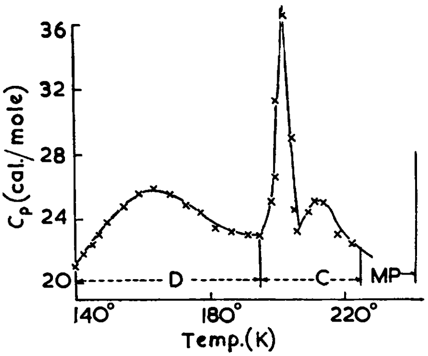


FIG. 8: 60·0 Moles % of $C_2H_4Cl_2$.

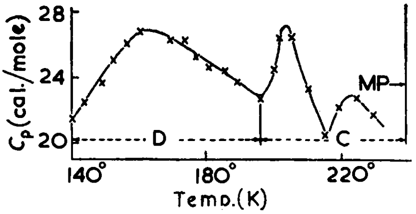


FIG. 9: 80·0 Moles % of $C_2H_4Cl_2$.

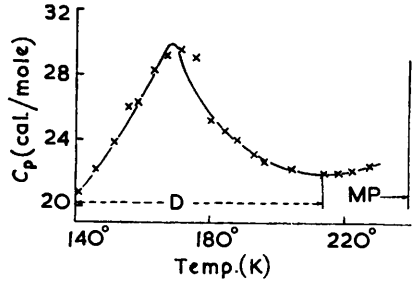


FIG. 10: 90·0 Moles % of $C_2H_4Cl_2$.

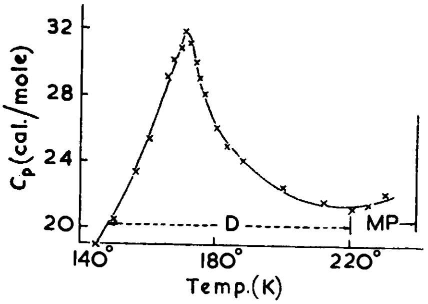
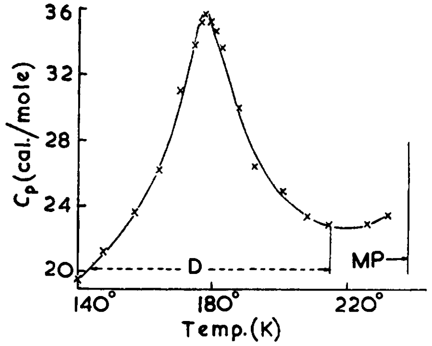


FIG. 11. Pure $C_2H_4Cl_2$.



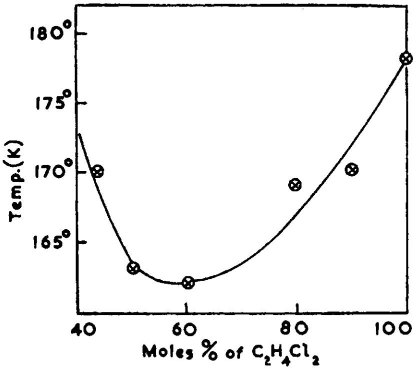


FIG. 12. *Variation of ethylene dichloride transition temperature with composition.*

DISCUSSION

Ethylene dichloride crystallises with a monoclinic space lattice containing two molecules per unit cell.[10] Infrared measurements [11] show the molecules to be in the *trans*-configuration, and *X*-ray and proton magnetic resonance results [12] indicate that the gradual transition at 178° K marks the onset of free rotation of the ethylene dichloride molecules without change of crystal structure. Ethylene dibromide has the same " β " crystal structure as the dichloride above its sharp transition at 250° K, but a different " α " form, also monoclinic but with four molecules per unit cell, below this temperature.[13] The

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[10] Milberg and Lipscomb, *Acta Cryst.*, 1951, **4**, 369; Reed and Lipscomb, *ibid.*, 1953, **6**, 45.

[11] Brown and Sheppard, *Trans. Faraday Soc.*, 1952, **48**, 128.

[12] Gutowsky and Pake, *J. Chem. Phys.*, 1950, **18**, 162.

[13] Meerman, Thesis, University of Utrecht, 1943.

dibromide molecules have the *trans*-configuration and are probably rotating as a whole, above 250° K.[11,14]

The sharp transition in pure ethylene dibromide is preceded by a seemingly anomalous rise in heat capacity, which Pitzer[8] suggested was the preliminary stage of a dichloride-type second-order rotational change. This change was more difficult for the dibromide than for the dichloride, was therefore delayed to a higher temperature, and before its completion gave place to a radical lattice change. In the light of the present information on crystal structures, which was not available to Pitzer, the only valid conclusion is that rotation is more difficult in the α dibromide lattice than in the β dichloride lattice.

Timmermans's observations of a continuous series of mixed crystals of ethylene dichloride and dibromide just below the freezing point is reasonable in the light of the crystal structures; although he did not report it, phase separation should occur at lower temperatures, to give a solid miscibility gap. When a mainly dibromide mixed crystal is cooled it will certainly undergo a lattice change at a temperature near that for pure dibromide, and at lower temperatures the dichloride molecules will be in an " alien " lattice. For a mainly dichloride mixed crystal there will be no such lattice change, and the dibromide molecules will always be in a lattice which is the stable one for dibromide at high enough temperatures. The solubility of dibromide in dichloride should therefore be considerably higher than that of dichloride in dibromide.

A further possibility is the formation of a super-lattice, most probably for mixed crystals with more or less equal proportions of each component. There might then be a Curie point, when the ordered low-temperature form passed into the disordered high-temperature form.

Because of these possible complications, only small additions of dibromide to pure dichloride, or *vice versa*, are likely to have a simple effect on phase transitions. Such replacement of the major component will change the lattice spacing and modify the lattice forces. The change in lattice forces will be due to (i) the attendant change in lattice spacing, (ii) the less symmetrical force field in the mixed crystal, and (iii) an actual change in intermolecular forces for a given distance. If the intermolecular forces are mainly dispersion forces they will be larger, the larger the molecules. If, however, carbon–halogen bond dipole attractions make an important contribution, replacement of dichloride by dibromide may result in a net reduction in intermolecular forces. The effect even of small replacements cannot, therefore, be readily predicted.

Region A (~250° K).—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 temperature according to the equation: $\Delta T = \boldsymbol{R}T^2n_2/n_1\Delta H$. This would indicate a lowering of about 8° for addition of 3 moles %, as against the observed lowering of less than 2°. The dichloride must, therefore, have a slight solubility in the low-temperature crystal, so that the above equation does not apply. The less symmetrical force-field in the mixed crystal should facilitate lattice transformation, which may not now be strictly isothermal. In fact, experiment shows it to be less sharp than in pure dibromide, as well as occurring at lower temperatures.

Region D (<178° K).—The unusual broadness of the rotational transition in pure ethylene dichloride presumably means that the forces opposing rotation are small, so that no drastic loosening of the inhibiting force-field occurs when the first few molecules begin to rotate. The dependence on composition of the temperature of the " dichloride " transition is shown in Fig. 12. The lowering of the transition temperature from 100 to 60 moles % of dichloride indicates a decrease of lattice forces when dichloride is replaced by dibromide, presumably because the reduction in dipole attractions outweighs the larger dispersion forces expected. The rise in transition temperature for less than 60

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[14] Ichishima and Mizushima, *J. Chem. Phys.*, 1950, **18**, 1420.

moles % of dichloride, and the accompanying change in the nature of the heat capacity anomaly, will be discussed in the next section in terms of super-lattice formation.

Region C (205—218° K).—The interconnected peaks near 210° K occur for neither of the pure compounds. They are unlikely to be due to straightforward rotational processes, since they have a shape and composition-dependence different from those of the peak in dichloride-rich mixtures. It is therefore suggested that the maximum at 206° K is due to a super-lattice transformation, which might occur in a molecular crystal when there has been a preliminary acquirement of rotational freedom. Any super-lattice anomaly will be most marked with roughly equimolecular mixtures, since the difference between ordered and disordered structures will then be greatest; so it is significant that the 206° peak is found only for mixtures with 40—60 moles % of dichloride and for the 18% mixture (discussed in the next section). Both its shape and its small dependence of temperature on composition are broadly similar to these factors for super-lattice changes in alloy systems.[15]

On this basis mixtures with more than 60 moles % of dichloride, with no peak at 206° K, have an essentially random arrangement of the two kinds of molecule at all temperatures, and the dichloride transition then almost certainly involves both kinds of molecule. With 40—60 moles % of dichloride there is a super-lattice at low temperatures, and the mutual isolation of the dichloride molecules, with relatively small coupling between them, may account for the facts that the dichloride transition temperature rises again in this range of composition and that the anomaly becomes smaller and more rounded in shape. It may even, in these circumstances, involve only dichloride molecules, or at least only a proportion of the dibromide molecules. In this case, desegregation as a result of the 206° K transition could conceivably facilitate the rotation of any non-rotating dibromide molecules and thus cause the smaller, subsidiary peak about 10° higher.

Region B (225—235° K).—The complex behaviour in this region for mixtures with 8 and 18 moles % of ethylene dichloride is best explained by the existence of a solid miscibility gap. If this gap is between ∼5 and ∼40 moles % of dichloride, mixed crystals falling outside these limits should remain homogeneous on cooling. Crystals of intermediate compositions should, however, separate into two components, with ∼5 and ∼40 moles % of dichloride. When such a mixture was heated, it would display the following features: (*a*) A transition or transitions around 210° K for the 40 moles % component, which might also show a dichloride-type transition at a lower temperature. The latter might well be undetectable, since it is only just apparent for the 43·5 moles % mixture. (*b*) One or more maxima, due to energy absorption on remixing to give a homogeneous mixed crystal. (*c*) A dibromide-type transition, at a temperature appropriate either to the homogeneous mixed crystal, or to a separated dibromide-rich component.

The critical (solid) solution temperature might well be just below the melting curve for the system, so that process (*a*) should certainly take place before any remixing. Processes (*b*) and (*c*), however, might occur at about the same temperature, so that here the picture would be more confused.

The complete separation and remixing hitherto assumed would probably not take place, but the annealing procedure should produce at least partial segregation into two mixed crystals, possibly in domains of limited extent, and there would then be some degree of remixing across the domain boundaries on heating. The course of events would then be more complex than already discussed, and several maxima might appear for process (*b*).

In fact, the mixture with 18 moles % of dichloride has peaks at 212° and 218° K, corresponding to those for the middle-range compositions. They are smaller than for the 44 moles % dichloride mixture, presumably because of the small amount of this component in the partially separated mixed crystals. Whether the isolated 216° K peak for 8 moles %

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[15] Sykes and Wilkinson, *J. Inst. Metals*, 1937, **61**, 223.

of dichloride is also due to a 40% component is more doubtful. This mixture has an unmistakable dibromide-type transition at 247° K, which is probably due to a 5 moles % component since it is only slightly lower than that for the 3 moles % mixture. That the 18 moles % mixture shows no dibromide-type peak is possibly because its melting temperature is lower than the expected dibromide transition temperature, even for a 5 moles % crystal. Confidence is therefore felt in attributing the broad features of the heat capacity curves for 8 and 18 moles % mixtures to a partial separation into two mixed crystals, even though it is impossible to analyse these curves in detail.

Summary.—Solid ethylene dibromide can dissolve up to about 5 moles % of ethylene dichloride. For less dichloride than this, the temperature of the sharp ethylene dibromide transition at 250° K is lowered, and the transition becomes less sharp, probably because the force-field in the mixed crystals is less symmetrical than in the pure dibromide.

Solid ethylene dichloride, on the other hand, can dissolve up to about 60 moles % of ethylene dibromide. Up to about 40 moles % of dibromide the replacement is random. The smaller dipole–dipole forces and larger lattice distances which result from the introduction of dibromide then progressively lower the temperature of the broad ethylene dichloride anomaly, though the heat-capacity maximum is as sharp as in pure dichloride. The anomaly is caused by the gradual onset of rotation of ethylene dichloride molecules in the pure compound, and of both kinds of molecule in the mixed crystals. From 40 to 60 moles % of ethylene dibromide, however, a super-lattice may be formed at low temperatures, and the mutual segregation of the two kinds of molecule may then account for the rise in the temperature of the dichloride transition as the proportion of dibromide increases. In this same composition range, the more rounded heat-capacity maximum may indicate that the onset of rotation now concerns only the ethylene dichloride molecules present. The heat-capacity maximum at about 206° K for mixtures in the 40—60 moles % range probably accompanies a super-lattice transformation, and above this temperature the distribution of ethylene dichloride and dibromide molecules is random. The small peak about 10° higher may be associated with the acquiring of rotational freedom by the ethylene dibromide molecules in the disordered crystals.

Finally, the existence of a solid miscibility gap at 5—40 moles % of ethylene dichloride results in the separation into two mixed crystals, containing respectively ~5 and ~40 moles % of ethylene dichloride, when crystals with overall compositions within this range are cooled. On heating, such systems display transitions characteristic of both the 5 and the 40 moles % crystals, and also additional heat-capacity maxima, which probably accompany a complete or partial remixing.

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