869. *Addition Compounds of Gallium Trichloride. Part IV.* The Thermal Stability and Heat of Formation of Gallium Trichloride–Phosphorus Trichloride.*

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Gallium trichloride and phosphorus trichloride form a 1 : 1 addition compound which melts incongruently at 28°. The heat of the reaction is 3·4 kcal. mole^{-1} at 25°; this corresponds to a heat of formation from the elements of 203·2 kcal. mole^{-1} for the equilibrium mixture of crystalline complex in the presence of its liquid dissociation products. The absence of any appreciable electrical conductivity in the system is interpreted in terms of an "ethane-like" structure $Cl_3Ga \leftarrow PCl_3$ for the complex which dissociates in the liquid state to give a solution of Ga_2Cl_6 in PCl_3.

The only recorded compounds in which phosphorus, arsenic, or antimony forms a direct donor–acceptor bond to gallium are the methyl derivatives Me_3Ga,XMe_3 (X = P, As, Sb).[1] Considerable interest attaches to such compounds because they afford a means of studying the interplay of several factors on bond strength and on the tendency to ionise. For example, the complex $Me_3Ga,AsMe_3$ (m. p. 23·5°)[1] may owe part of its stability to the heteropolarity of the Ga–As bond, since it is isoelectronic with the unknown hexamethyl-digermane Ge_2Me_6 (though it is not certain that hexamethyldigermane could not be prepared, for the hexaethyl derivative is a stable compound). The possibility of inter-action between the trihalides of these elements introduces a further factor, for the gallium trihalides, unlike trimethylgallium, are dimeric and the formation of an adduct involves the preliminary breaking of two halogen bridge bonds with consequent reduction in stability. Thus, despite the existence of hexachlorodisilane (Si_2Cl_6) there is no inter-action between aluminium trichloride (Al_2Cl_6) and phosphorus trichloride to give the isoelectronic complex $AlCl_3,PCl_3$. However, replacement of aluminium trichloride by gallium trichloride increases the disparity in electropositivity of the donor and acceptor atoms and also lowers the dimerisation energy of the acceptor molecule, thus permitting the formation of an unstable complex $GaCl_3,PCl_3$. The present work was undertaken to in-vestigate whether this complex has an ethane-like structure with a covalent Ga–P bond, or whether the difference in electropositivity of gallium and phosphous was sufficient to result in an ionic complex such as aluminium tribromide–antimony tribromide.[2]

EXPERIMENTAL AND RESULTS

Phosphorus trichloride was purified by fractionation in a 50-cm. column packed with glass helices and was handled thereafter in a vacuum line. Gallium trichloride was prepared and purified as described in Part I[3] which also outlined the techniques used to obtain the melting-point data. The heat of reaction was determined by use of the calorimeter described in Part III.[4] The circuit used to measure the electrical conductivity at 1000 cycles/sec. has also been described previously.[5]

When successive amounts of phosphorus trichloride are distilled on to gallium trichloride, the m. p. of the system drops steadily as indicated in Table 1. The results are plotted in the Figure which shows the presence of a 1 : 1 addition compound melting incongruently at 28°.

The heat of reaction of 1 mole of crystalline gallium trichloride with one mole of liquid phosphorus trichloride to give a two-phase mixture of solid addition compound in equilibrium

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* The paper, *J. Inorg. Nuclear Chem.*, 1957, **4**, 291, is regarded as Part III.

[1] Coates, *J.*, 1951, 2003.

[2] Isbekow, *Z. anorg. Chem.*, 1926, **158**, 87; Gorenbein, *Zhur. obshchei Khim.*, 1948, **18**, 1427, and refs. therein.

[3] Greenwood and Wade, *J.*, 1956, 1527.

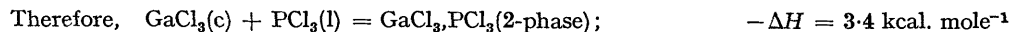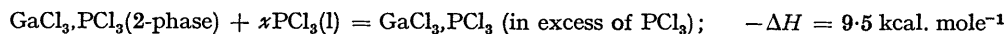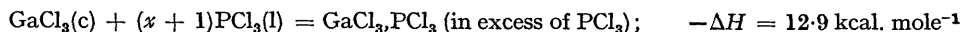[4] Greenwood and Perkins, *J. Inorg. Nuclear Chem.*, 1957, **4**, 291.

[5] Greenwood and Worrall, *ibid.*, 1957, **3**, 357.

TABLE 1. *Melting point of the system gallium trichloride–phosphorus trichloride.*

PCl_3 (mole %)	0·0	1·5	5·8	9·1	12·3	17·4	21·8	24·5	29·9	33·7	37·5	41·5	44·6
M. p.	77·8°	77·2°	75°	72·5°	70·5°	67°	63·5°	60°	55·5°	52°	47°	42°	38·5°
PCl_3 (mole %)	47·4	49·7	54·1	57·0	58·9	61·4	65·3	69·1	75·9	83·8	86·6	100·0	
M. p.	34°	32°	27°	25·5°	23°	20°	16°	11°	1·5°	−13·5° *	−21·5° *	−90°	

* and a eutectic at −93°.

with its liquid dissociation products at 25° was obtained from the heats of solution of gallium trichloride and of the complex in phosphorus trichloride:

$$GaCl_3(c) + (x + 1)PCl_3(l) = GaCl_3,PCl_3 \text{ (in excess of } PCl_3); \quad -\Delta H = 12·9 \text{ kcal. mole}^{-1}$$

$$GaCl_3,PCl_3(\text{2-phase}) + xPCl_3(l) = GaCl_3,PCl_3 \text{ (in excess of } PCl_3); \quad -\Delta H = 9·5 \text{ kcal. mole}^{-1}$$

$$\text{Therefore,} \quad GaCl_3(c) + PCl_3(l) = GaCl_3,PCl_3(\text{2-phase}); \quad -\Delta H = 3·4 \text{ kcal. mole}^{-1}$$

The supporting thermochemical data are presented in Tables 2 and 3. It should perhaps be emphasised that the precise chemical constitution of the final state in the solution reactions is

TABLE 2. $GaCl_3$ (c) + *excess of* PCl_3 (l) = $GaCl_3,PCl_3$ (*in excess of* PCl_3).

PCl_3 (g.)	$GaCl_3$ (g.)	Mole ratio	$\Delta T(\mu v)$	Calibration (cal. per μv)	$-\Delta H$ (kcal. mole^{-1})
150 g.	0·0713	2700 : 1	69·0	0·0759	12·9$_5$
150 g.	0·0668	2880 : 1	66·0	0·0742	12·9$_2$
					Mean 12·9$_4$

TABLE 3. $GaCl_3,PCl_3$ (*2-phase*) + *excess of* PCl_3(l) = $GaCl_3,PCl_3$ (*in excess of* PCl_3).

PCl_3 (g.)	$GaCl_3,PCl_3$ (g.)	Mole ratio	$\Delta T(\mu v)$	Calibration (cal. per μv)	$-\Delta H$ (kcal. mole^{-1})
190 g.	0·2484	1740 : 1	89·0	0·0853	9·5$_5$
192 g.	0·7724	567 : 1	264·0	0·0892	9·5$_3$
					Mean 9·5$_4$

immaterial provided that it is the same for both reactions so that Hess's law can be applied. It has been specified in the equations as " $GaCl_3,PCl_3$ (in excess of PCl_3) " for convenience but it might equally well have been written as " $\frac{1}{2}Ga_2Cl_6$ in $(x + 1)PCl_3$ " or even non-committally as "final state."

PCl_3 (mole %)
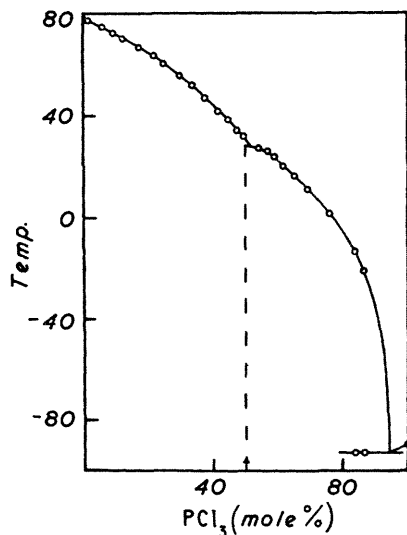
DISCUSSION

The very small value (3·4 kcal. mole^{-1}) for the interaction of gallium trichloride with phosphorus trichloride at 25° implies that the complex is unstable with respect to dissociation into its donor and acceptor components, for the decrease in entropy during the reaction might reasonably be expected to be about 10—15 cal. deg.$^{-1}$ mole^{-1}, so that the free-energy change ($-\Delta G = -\Delta H + T\Delta S = 3400 - 300|\Delta S|$) would be approximately zero or slightly negative, implying a fairly evenly balanced equilibrium between the complex and its components.

The standard heat of formation of the equilibrium mixture containing the dissociating incongruent compound can be estimated from the known heats of formation of $GaCl_3(c)$ [6] and $PCl_3(l)$; [7] these are 125·4 and 74·4 kcal. mole^{-1} respectively and lead to a value of $-\Delta H_f°$ ($GaCl_3,PCl_3$: two-phase) $= 203·2$ kcal. mole^{-1}. There is little point in trying to

[6] Klemm and Jacobi, *Z. anorg. Chem.*, 1932, **207**, 177.
[7] Neale and Williams, *J.*, 1954, 2156.

evaluate.the corresponding heat for the gas-phase reaction since the complex is completely dissociated even in the liquid phase.

The simplest structure for the solid complex gallium trichloride–phosphorus trichloride is the ethane-like model $Cl_3Ga \leftarrow PCl_3$. The only comparable compound containing a gallium–phosphorus bond is $Me_3Ga \leftarrow PMe_3$; this melts at $56 \cdot 5°$ and has an extrapolated b. p. of $173°$.[1] Its greater stability is indicated by the fact that it is less than 10% dissociated in the vapour phase at $100°$ and has a heat of dissociation of 18 kcal. mole^{-1}. The incongruent melting point of the chlorine derivative implies complete dissociation in the liquid phase at room temperature. This is confirmed by a preliminary investigation of the Raman spectra carried out in collaboration with Dr. L. A. Woodward and Mr. R. Taylor, who found, qualitatively, that only the lines of the parent species Ga_2Cl_6 and PCl_3 were present in a solution of approximate composition $GaCl_3 + 2PCl_3$.

Absence of any appreciable ionic dissociation in the system was demonstrated by measurement of the electrical conductivity of a 1 : 1 mixture of the components prepared by the vacuum-line techniques previously described.[8] At $25°$, the specific conductivity was $2 \cdot 87 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ and this increased as the temperature was raised in the range up to $75°$ with an activation energy for conduction of about 6 kcal. mole^{-1}. Partial freezing of the complex decreased the conductivity more than twofold. The conductivity of phosphorus trichloride was $<4 \times 10^{-8}$ ohm^{-1} cm.$^{-1}$; that of gallium trichloride is $1 \cdot 86 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ at $78°$.[5]

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[8] Greenwood and Wade, *J.*, 1957, 1516.