# 291. *Addition Compounds of Gallium Trichloride. Part II.*[1] *Gallium Trichloride–Phosphorus Oxychloride.*

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The melting-point diagram of the system gallium trichloride–phosphorus oxychloride shows the presence of a new compound, $GaCl_3,POCl_3$, m. p. 118·5°, and the possible formation of a second compound $GaCl_3,2POCl_3$ melting incongruently at about 77°. The 1 : 1 compound has a vapour pressure of $<1$ mm. at the melting point and can be sublimed *in vacuo* without decomposition. The specific electrical conductivity, viscosity, density, and surface tension of the molten compound have been determined over a range of temperature in order to calculate the molar conductivity, reduced conductivity, activation energy of conduction, activation energy of viscous flow, molar surface free energy, parachor, and related properties. Direct-current current–voltage experiments have also been carried out. It is suggested that chlorine rather than oxygen is the donor atom and that the complex is dissociated to the extent of about ½% into the ions $POCl_2^+$ and $GaCl_4^-$. The results are compared with those obtained on other systems in which phosphorus oxychloride is the ligand.

Physical properties of the new compound gallium trichloride–phosphorus oxychloride, which is formed rapidly and exothermally by gallium trichloride in the presence of phosphorus oxychloride vapour, are reported. The complex melts to give a stable liquid of moderately high electrical conductivity and is ideally suited to physicochemical studies. Its properties are compared with those of other gallium trichloride addition compounds and with other complexes in which phosphorus oxychloride is the ligand. It is considered to ionise as $POCl_2^+GaCl_4^-$.

## Experimental and Results

Gallium trichloride was prepared and purified as described in Part I.[1] Phosphorus oxychloride was fractionated in an efficient column and then vacuum distilled. Mixtures of known composition for the phase diagram were prepared by the techniques used for the system with acetyl chloride.[1] Gallium trichloride absorbed phosphorus oxychloride spontaneously and with considerable evolution of heat up to 49 moles % of $POCl_3$; thereafter, further phosphorus oxychloride was condensed from the vacuum line by cooling the reaction vessel in alcohol–solid carbon dioxide. There was a slight initial attack on the Apiezon M tap grease but this had no apparent effect on the results.

Pure gallium trichloride–phosphorus oxychloride was prepared on the 50 g. scale by absorbing the required weight of phosphorus oxychloride *in vacuo* on a known weight of resublimed gallium trichloride at *ca.* 120°. The compound which had the correct composition to within 1 part in 8000 by weight, was a white solid which melted to a clear, colourless liquid.

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[1] Part I, Greenwood and Wade, *J.*, 1956, 1527.

The electrical conductivity of the molten compound was measured at 1000 c./sec. with the circuit previously described.[2] The cell, shown in Fig. 1, was of soda-glass with platinum electrodes sealed through sleeves of cobalt glass. The volume to the etched mark was 9·5 ml. and the cell constant was 0·9152 cm.$^{-1}$. The resistance, which varied between 500 and 700 ohms, was measured to within 1 part in 3000. The side arms were sealed at atmospheric pressure to restrict the otherwise violent movement of the mercury contacts during handling. A graded seal, *C*, connected the soda-glass cell to the Pyrex-glass loading unit. The complex was sealed into the wide entry tube *A*, the apparatus evacuated through section *D*, and the complex melted, run into the crystallisation bulbs *B* and degassed, after which the apparatus was sealed at points 1 and 2. The remaining central unit was inverted and the compound fractionally crystallised five times by being melted at 125° and cooled at 112°, about one fifth of the solidifying liquid being rejected in each cycle. The m. p. did not rise appreciably during this process and the final purified sample melted at 118·5°. The pure compound was run into the cell for a preliminary conductivity measurement. With the fractionation bulbs outside the thermostat, but still connected to the cell, the conductivity increased slowly by 6% over a period of 8 hr. at 127°, most of this increase occurring during the first 2 hr. The compound was returned to the double-bulb unit and fractionally recrystallised again but the effect persisted: the conductivity, initially close to the first values on the preceding run, increased by 4% in 3½ hr. and 5% in 6½ hr. Further experiments showed that constant values could only be obtained when the cell was sealed off at point 3 and totally immersed in the thermostat. The increase in conductivity in the earlier experiments was presumably due either to the slow irreversible evaporation of one of the components from the complex or, more probably, to the reabsorption *via* the vapour phase of some component initially rejected in the fractional crystallisation. When the conductivity was measured in an isolated, totally immersed cell, it remained constant to within 0·1% during several hours at 127°.

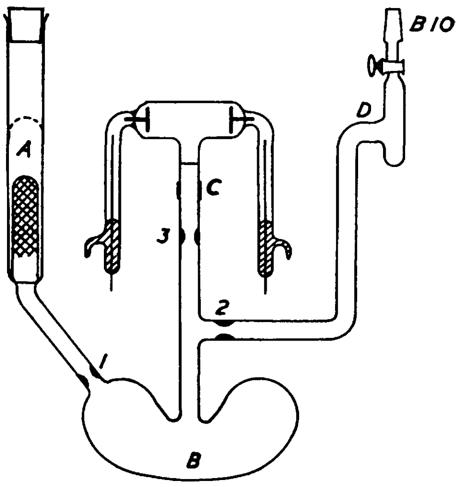

FIG. 1. *Conductivity cell.*

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

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $POCl_3$ (mole %) ... | 0·0 | 2·6 | 6·2 | 8·7 | 11·8 | 14·2 | 17·5 | 21·8 | 23·8 |
| M. p. .................. | 77·8° | 76·5° | 74° | 70° | 65° | 60° | 52° * | 36° * | 26° * |
| $POCl_3$ (mole %) ...... | 25·0 | 28·3 | 31·4 | 34·3 | 37·9 | 39·4 | 42·1 | 45·6 | 49·2 |
| M. p. .................. | 18° * | 30° * | 54° * | 68·5° * | 83° | 87° | 96° | 107° | 117·5° |
| $POCl_3$ (mole %) ...... | 50·8 | 53·4 | 58·6 | 63·1 | 65·8 | 68·7 | 70·7 | 73·0 | 76·6 |
| M. p. .................. | 117·5° | 113° | 102° | 90° | 82° | 74° | 69° | 63° | 53° |
| $POCl_3$ (mole %) ...... | 80·0 | 82·4 | 84·3 | 86·0 | 87·1 | 88·9 | 90·9 | 100·0 | |
| M. p. .................. | 42° | 33° † | 23° † | 15° † | 9° † | −1° † | −3° † | +1 | |

* And a eutectic at +1°. † And a eutectic at −4°.

Viscosity was measured in an all-glass, sealed, capillary viscometer[3] which was loaded as described elsewhere.[4] For the instrument used, the kinematic voscosity, $\nu$ (centistokes), was related to the efflux time, $t$ (sec.), by the equation $\nu = 1{\cdot}8771 \times 10^{-2}t - 5{\cdot}44t^{-1}$. $t$ varied between 50 and 68 sec., which is rather shorter than desirable, but experiments with water, which has a similar efflux time at room temperature, showed that the instrument was still behaving normally even though the second term in the above expression amounted to 10% of the first. However, the timing errors in individual runs were increased to about 0·2%. For

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[2] Greenwood and Worrall, *J. Inorg. Nuclear Chem.*, in the press.
[3] Greenwood and Wade, *J. Appl. Chem.*, in the press.
[4] *Idem, J. Inorg. Nuclear Chem.*, in the press.

this reason, the mean of six readings was taken at each temperature, the separate readings agreeing to 0·1 sec.

Density and surface tension were measured in the two-capillary dilatometer as already described.[4] The instrument was loaded *via* a double-bulb fractional recrystallisation unit.

*Results.*—The melting points in the system gallium trichloride–phosphorus oxychloride are summarised as a function of composition in Table 1. Fig. 2 shows that there is a maximum of 118·5° at the 1 : 1 ratio and eutectics at $-1°$ (26·3 mole % of $POCl_3$) and $-4°$ (89·5% of $POCl_3$). The compound $GaCl_3,POCl_3$ melts at 118·5° without decomposition and has a vapour pressure of $<1$ mm. at the m. p. (cf. $GaCl_3$,63 mm.[5, 6] and $POCl_3$, 1123 mm.[7] at 118·5°). The diagram also indicates a second compound, $GaCl_3,2POCl_3$, melting incongruently at about 77°, but this compound must be considered as less definite until further evidence for its existence is obtained from other property–composition diagrams.

TABLE 2. *Electrical conductivity of* $GaCl_3,POCl_3$ *between* 118° *and* 148°.

| No. | $t$ | $10^3\kappa$ (ohm$^{-1}$ cm.$^{-1}$) | $\mu = \kappa V_M$ (cm.$^2$ ohm$^{-1}$) | $\mu\eta$ (cm.$^2$ CP ohm$^{-1}$) |
|---|---|---|---|---|
| 11 | 118·6° | 1·263 | 0·2273 | 0·442 |
| 10 | 119·0 | 1·270 | 0·2286 | 0·442 |
| 12 | 119·6 | 1·280 | 0·2305 | 0·443 |
| 9 | 120·0 | 1·287 | 0·2319 | 0·444 |
| 13 | 120·6 | 1·296 | 0·2337 | 0·444 |
| 8 | 121·0 | 1·305 | 0·2354 | 0·445 |
| 14 | 121·6 | 1·314 | 0·2370 | 0·446 |
| 7 | 122·0 | 1·321 | 0·2384 | 0·446 |
| 15 | 122·6 | 1·331 | 0·2405 | 0·447 |
| 6 | 123·0 | 1·337 | 0·2414 | 0·447 |
| 16 | 123·6 | 1·349 | 0·2437 | 0·448 |
| 5 | 124·0 | 1·355 | 0·2449 | 0·449 |
| 17 | 124·6 | 1·367 | 0·2471 | 0·449 |
| 4 | 125·0 | 1·372 | 0·2482 | 0·450 |
| 18 | 125·6 | 1·385 | 0·2505 | 0·451 |
| 3 | 126·0° | 1·390 | 0·2517 | 0·451 |
| 19 | 126·6 | 1·402 | 0·2540 | 0·452 |
| 1 | 127·0 * | 1·408 | 0·2552 | 0·452 |
| 2 | 127·0 † | 1·406 | 0·2548 | 0·451 |
| 20 | 127·0 ‡ | 1·408 | 0·2552 | 0·452 |
| 21 | 127·6 | 1·420 | 0·2575 | 0·453 |
| 22 | 128·0 | 1·427 | 0·2587 | 0·454 |
| 30 | 130·6 | 1·474 | 0·2680 | 0·457 |
| 23 | 133·0 | 1·521 | 0·2770 | 0·461 |
| 29 | 135·6 | 1·574 | 0·2874 | 0·464 |
| 24 | 138·0 | 1·617 | 0·2959 | 0·468 |
| 28 | 140·6 | 1·672 | 0·3065 | 0·471 |
| 25 | 143·0 | 1·718 | 0·3156 | 0·474 |
| 27 | 145·6 | 1·766 | 0·3251 | 0·477 |
| 26 | 148·0 | 1·827 | 0·3370 | 0·480 |

* + 0 hour; † + 2 hours; ‡ + 5 hours.

The specific electrical conductivity, $\kappa$ (ohm$^{-1}$ cm.$^{-1}$) of the 1 : 1 compound between the m. p. and 148° is given in Table 2 which also lists the molar conductivity, $\mu = M\kappa/d = \kappa V_M$, and the molar conductivity reduced to unit viscosity, $\mu\eta$. Molten gallium trichloride–phosphorus oxychloride is seen to be a moderately good conductor: at the m. p. the specific conductivity is $1{\cdot}261 \times 10^{-3}$ ohm$^{-1}$ cm.$^{-1}$ and this corresponds to a molar conductivity of 0·2270 cm.$^2$ ohm$^{-1}$ and a reduced conductivity of 0·442 cm.$^2$ CP ohm$^{-1}$. In order to check that the drift in conductivity discussed in the experimental section had been eliminated, measurements were taken at 1° intervals between 127° and 119° (● on Fig. 3) and then at 1° intervals between 118·6° and 127·6° with a check reading at 127·0° (○ on Fig. 3). The run was then extended to 148° in 5° intervals (○), followed by a downward run (▲) in 5° intervals from 145·6°. It is clear that the results are reproducible even after the complex has been heated 30° above its m. p. The plot of log $\kappa$ against $1/T°$ (K) which is shown in Fig. 3 is straight over the entire range, and corresponds to an activation energy $E_\kappa$ of $4{\cdot}09_5$ kcal. mole$^{-1}$.

A D.C. current–voltage experiment carried out at 127° indicated two discontinuities corresponding to decomposition potentials of 1·10 and 1·58 V.

At currents greater than about 4 mA there was some blackening of the cathode surface which tended to increase the electrical capacity of the cell but there were no gaseous products of electrolysis. In a separate series of experiments an approximate value of the back-e.m.f. was obtained by electrolysing the molten compound for 1 min. at 5 mA and then measuring the cell voltage directly. In these conditions the electrolysis products rapidly diffused away from the electrodes and the voltmeter also drew current from the cell so that the observed e.m.f. fell rapidly with time. In a typical experiment the back-e.m.f. of about 1·0 V dropped to 0·9 V in 6 sec. after the cessation of electrolysis, to 0·5 V in 10 sec., and to 0·33 V in 60 sec.

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[5] Laubengayer and Schirmer, *J. Amer. Chem. Soc.*, 1940, **62**, 1578.

[6] Fischer and Jübermann, *Z. anorg. Chem.*, 1936, **227**, 227.

[7] Arii, *Sci. Reports Tôhoku Imp. Univ.*, Ser. I., 1933, **22**, 182; *Chem. Abs.*, 1933, **27**, 3865.

FIG. 2. *Phase diagram of the system gallium trichloride–phosphorus oxychloride.*

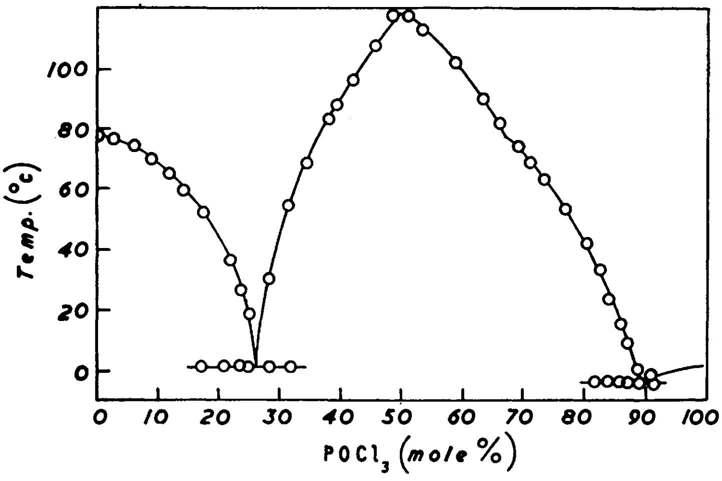
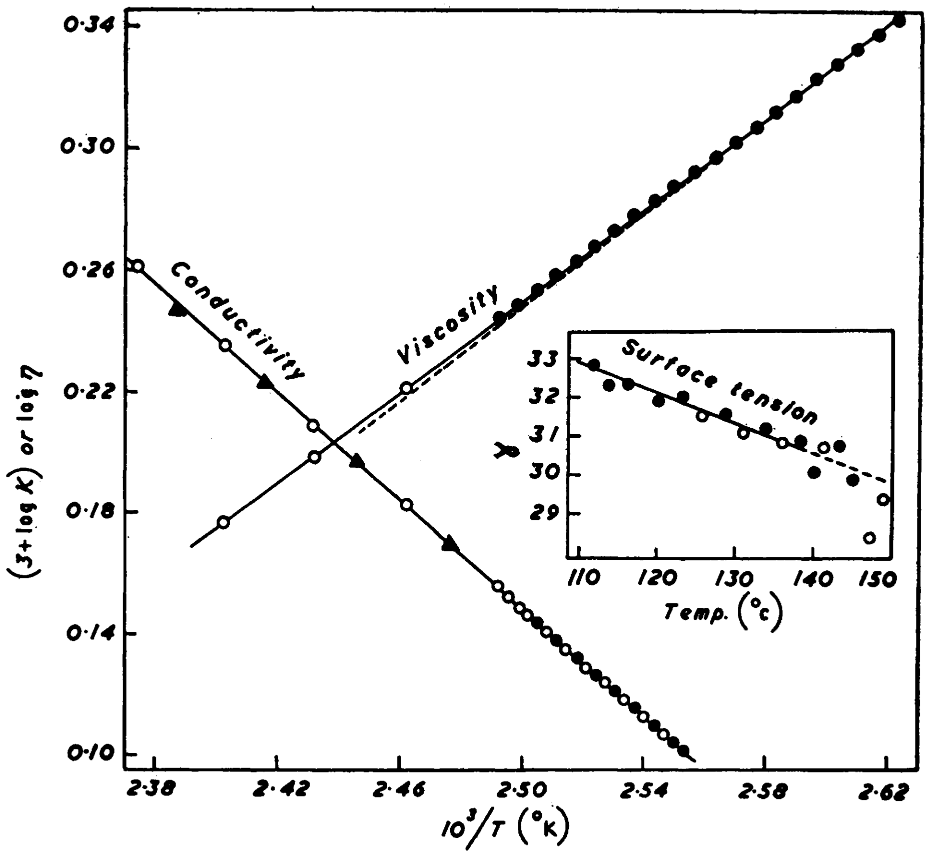


FIG. 3. *Conductivity, viscosity, and surface tension of the system gallium trichloride–phosphorus oxychloride.*



This suggests that the decomposition potential, measured as 1·10 v, is not seriously influenced by overvoltage and so may be taken as an indication of the free energy change of the cell reaction.

The viscosity results are set out in Table 3. Measurements were started at 128° and then taken at 1° intervals down to 108° at which temperature the complex had supercooled more than 10°. The kinematic viscosities ($\nu$ cs) so obtained were converted to dynamic viscosities ($\eta$ cP) and plotted logarithmically (●) in Fig. 3. Further results at 5° intervals between 128° and 143° are plotted as (○). It appears that there is a small, discontinuous change in slope at about 117°: the activation energy increases by 4·5% from $E_{\eta} = 3{\cdot}41_4$ kcal. mole$^{-1}$ above the m. p. to $3{\cdot}56_7$ kcal. mole$^{-1}$ below it. At 118·5° the kinematic viscosity is 1·064 cs, almost exactly the same as that of water at 18°; the dynamic viscosity is 1·947 cP which is nearly twice that of water at 18° because of the higher density of the complex.

The density and molar volume of gallium trichloride–phosphorus oxychloride from 111° to 149° are shown in Table 4. The density can be represented with a standard deviation of 1·6 in the last decimal place by the equation $d_4^t = 1{\cdot}8281 - [1{\cdot}526 \times 10^{-3} (t - 120)]$.

The surface tension, which was measured simultaneously with the density, was less precise as the capillary diameters were rather larger than the optimum values: narrower tubes would increase the difficulty of loading the dilatometer and would limit the temperature range over which the density could be conveniently studied in a reasonably sized thermostat. Nevertheless, the results give a useful indication of the surface tension and related properties of the complex. The values obtained are summarised in Table 4 and Fig. 3. In calculating these values, a meniscus correction appropriate to capillaries of approximately 1 mm. diameter was applied; this relates the observed capillary rise, $h_0$, to the true capillary rise, $h$, and the radius, $r$, by means of the equation $h = h_0 + (r/3) - (0{\cdot}1288r^2/h_0) + (0{\cdot}1312r^3/h_0^2)$. The correction was about 2% of the value of the surface tension. Below 140° the surface tension is given with a standard deviation of 0·13 dyne cm.$^{-1}$ by the relation $\gamma = 32{\cdot}0 - 0{\cdot}076(t - 120)$. Above 140° the results are somewhat erratic. The molar surface free energy $\omega$ (erg mole$^{-2/3}$), calculated from the experimental points, is also listed in Table 4; below 140° it can be represented by $\omega = 1022 - 1{\cdot}81(t - 120)$, where 1·81 is the Eötvös constant $k$. A very approximate idea of the critical temperature may be obtained

TABLE 3. *Viscosity of molten and supercooled* $GaCl_3,POCl_3$ *between* 108° *and* 143°.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $t$ ............ | 108·0° | 109·0° | 110·0° | 111·0° | 112·0° | 113·0° | 114·0° | 115·0° |
| $\nu$ (cs) ...... | 1·194 | 1·180 | 1·167 | 1·154 | 1·142 | 1·128 | 1·115 | 1·104 |
| $\eta$ (cP) ...... | 2·205 | 2·178 | 2·152 | 2·125 | 2·102 | 2·075 | 2·049 | 2·027 |
| $t$ ............ | 116·0° | 117·0° | 118·0° | 119·0° | 120·0° | 121·0° | 122·0° | 123·0° |
| $\nu$ (cs) ...... | 1·092 | 1·080 | 1·069 | 1·058 | 1·047 | 1·037 | 1·026 | 1·015 |
| $\eta$ (cP) ...... | 2·003 | 1·979 | 1·958 | 1·936 | 1·914 | 1·894 | 1·872 | 1·852 |
| $t$ ............ | 124·0° | 125·0° | 126·0° | 127·0° | 128·0° | 133·0° | 138·0° | 143·0° |
| $\nu$ (cs) ...... | 1·005 | 0·994 | 0·985 | 0·975 | 0·965 | 0·921 | 0·878 | 0·838 |
| $\eta$ (cP) ...... | 1·831 | 1·809 | 1·791 | 1·711 | 1·753 | 1·666 | 1·581 | 1·503 |

TABLE 4. *Density and surface tension of molten* $GaCl_3,POCl_3$ *between* 111° *and* 149°.

| No. | $t$ | $d_4^t$ (g. ml.$^{-1}$) | $V_M$ (ml. mole$^{-1}$) | $\gamma$ (dyne cm.$^{-1}$) | $\omega = \gamma V_M^{2/3}$ | $[P]$ |
|---|---|---|---|---|---|---|
| 17 | 111·6° | 1·8410 | 178·95 | 32·7 | 1040 | 428·0 |
| 16 | 113·8 | 1·8374 | 179·29 | 32·3 | 1027 | 427·4 |
| 15 | 117·0 | 1·8323 | 179·79 | 32·3 | 1029 | 428·6 |
| 14 | 120·0 | 1·8281 | 180·21 | 31·8 | 1015 | 428·0 |
| 13 | 123·1 | 1·8233 | 180·68 | 32·0 | 1022 | 429·6 |
| 1 | 125·9 | 1·8192 | 181·09 | 31·6 | 1010 | 429·1 |
| 12 | 128·7 | 1·8148 | 181·53 | 31·5 | 1009 | 429·9 |
| 2 | 131·1 | 1·8112 | 181·89 | 31·1 | 998 | 429·5 |
| 11 | 133·7 | 1·8071 | 182·30 | 31·1 | 999 | 430·4 |
| 3 | 136·1 | 1·8037 | 182·64 | 30·8 | 990 | 430·1 |
| 10 | 138·1 | 1·8005 | 182·97 | 30·8 | 991 | 430·9 |
| 9 | 140·0 | 1·7975 | 183·27 | 30·0 | 967 | 428·8 |
| 4 | 141·4 | 1·7956 | 183·47 | 30·6 | 989 | 431·6 |
| 8 | 143·1 | 1·7930 | 183·73 | 30·7 | 992 | 432·4 |
| 7 | 145·0 | 1·7903 | 184·01 | 29·8 | 963 | 429·8 |
| 5 | 147·1 | 1·7869 | 184·36 | 28·3 | 917 | 425·3 |
| 6 | 149·0 | 1·7840 | 184·66 | 29·3 | 950 | 429·6 |

from this expression on the assumption that the linear relation holds until the molar surface free energy becomes zero. This leads to a critical temperature of 685° and a boiling point of approximately 365° if the b. p. is taken as 2/3 of the critical temperature on the absolute scale.

The parachor values ($[P] = V_M\gamma^{\frac{1}{4}}$) calculated from the molar volume and surface tension are also listed in Table 4. As the vapour pressure of the complex is only of the order of 1 mm. at these temperatures the neglect of the gas density has negligible effect on the calculation. Between 111° and 140° the parachor has a mean value of 429·2 with a standard deviation of ±1·1. The six readings above 140° give a mean value of 429·6 but with a standard deviation of 2·5. The average of all values is 429·3 ± 1·6. The value calculated by McGowan's method,[8] by use of the predicted value of 99·0 for the parachor of gallium, is 428·7 in excellent agreement with the observed value.

## DISCUSSION

Gallium trichloride and phosphorus oxychloride form a 1 : 1 addition compound which melts at 118·5° to give a stable, colourless liquid. Its properties in the molten state at 118·5° are summarised in Table 5 which also lists the corresponding properties of the donor and acceptor moieties at their respective m. p.s. A further comparison of the three compounds all at 118·5° is also given, the values for gallium trichloride and phosphorus oxychloride being recorded in parentheses after the figures referring to data at the m. p. It is seen that complex formation is accompanied by an appreciable increase in the m. p. and b. p. of the system, the values for the complex being above those of both

TABLE 5. *Comparison of the properties of* $Ga_2Cl_6$, $GaCl_3,POCl_3$, *and* $POCl_3$ *at their respective m. p.s.*

| Property | $Ga_2Cl_6$ (a) | $GaCl_3,POCl_3$ | $POCl_3$ |
|---|---|---|---|
| Mol. wt. | $2 \times 176{\cdot}09$ | 329·44 | 153·35 |
| M. p. | 77·75° | 118·5° | 1° |
| B. p. | 200° | est. 365° | 105° |
| $p$ (mm. Hg) | 10·4 (j) (63) (j) | $<1$ | 11·0 (k) (1123) (k) |
| $d$ (g. ml.$^{-1}$) | 2·0536 (1·9685) | 1·8304 | 1·7104 (b) (1·4930) (b) |
| Temp. coef. of $d$ | $2{\cdot}09 \times 10^{-3}$ | $1{\cdot}526 \times 10^{-3}$ | $1{\cdot}85 \times 10^{-3}$ |
| $V_M$ (ml. mole$^{-1}$) | $2 \times 85{\cdot}72$ (89·45) | 179·98 | 89·66 (b) (102·71) (b) |
| $\nu$ (cs) | 0·8877 (0·539) | 1·064 | 0·866 (c) (0·36) (d) |
| $\eta$ (cP) | 1·823 (1·061) | 1·947 | 1·465 (c) (0·53) (d) |
| $E_\eta$ (kcal. mole$^{-1}$) | $3{\cdot}63_6$ | $3{\cdot}41_4$ | $\sim$1·90 (e) |
| $\phi$ (cP$^{-1}$) | 0·5486 (0·943) | 0·5137 | 0·683 (c) (1·89) (d) |
| $B$ (ml. cP g.$^{-1}$) | $5{\cdot}75 \times 10^{-2}$ | $7{\cdot}89 \times 10^{-2}$ | $6{\cdot}45 \times 10^{-2}$ (f) |
| $\gamma$ (dyne cm.$^{-1}$) | 27·3 (23·1) | 32·1 | 34·5 (g) (20·1) (g) |
| Temp. coef. of $\gamma$ | 0·105 | 0·076 | 0·122 (g) |
| $\omega$ (erg mole$^{-2/3}$) | 842·5 (732·4) | 1025 | 686·6 (g) (440·8) (g) |
| $k$ (Eötvös) | 2·70 | 1·81 | 2·20 (g) |
| $[P]$ | 395·5 (calc. 418·0) | 429·2 (calc. 428·7) | 217·6 (g) (calc. 219·7) |
| $\kappa$ (ohm$^{-1}$ cm.$^{-1}$) | $1{\cdot}86 \times 10^{-6}$ (h) ($2{\cdot}0 \times 10^{-6}$) | $1{\cdot}261 \times 10^{-3}$ | $1{\cdot}25 \times 10^{-6}$ (i) ($2{\cdot}3 \times 10^{-6}$) (i) |
| $E_\kappa$ (kcal. mole$^{-1}$) | — | $4{\cdot}09_5$ | — |
| $\mu$ (cm.$^2$ ohm$^{-1}$) | $1{\cdot}6 \times 10^{-4}$ ($1{\cdot}8 \times 10^{-4}$) | 0·2270 | $1{\cdot}13 \times 10^{-4}$ (i) ($2{\cdot}2 \times 10^{-4}$) (i) |
| $\mu\eta$ (cm.$^2$ cP ohm$^{-1}$) | $2{\cdot}9 \times 10^{-4}$ ($1{\cdot}9 \times 10^{-4}$) | 0·442 | $1{\cdot}6 \times 10^{-4}$ (i) ($1{\cdot}2 \times 10^{-4}$) (i) |

[a] Taken or calc. from data in ref. 4. [b] Values from Bowden and Morgan (*Phil. Mag.*, 1940, **29**, 367) which are concordant with those of Ramsay and Shields (*J.*, 1893, **63**, 1089) and Sugden, Reed, and Wilkins (*J.*, 1925, 1525) but disagree with more recent results of Gutmann (*Monatsh.*, 1952, **83**, 164) which are apparently in error by *ca.* 1%. [c] Gutmann (*loc. cit.*) and Lutschinsky (*Z. anorg. Chem.*, 1935, **223** ,210); Bowden and Morgan (*loc. cit.*) give $\nu = 0{\cdot}883$ cs, $\eta = 1{\cdot}510$ cP, and $\phi = 0{\cdot}662$ cP$^{-1}$ at 1°. [d] By logarithmic extrapolation of data by Gutmann (*loc. cit.*). [e] Data by Bowden and Morgan (*loc. cit.*) give a linear plot of slope 1·92 kcal. mole$^{-1}$. Activation energies calculated from data by Gutmann and Lutschinsky (*locc. cit.*) decrease from 2·09 and 2·16 kcal. mole$^{-1}$ respectively near the m. p. to 1·68 and 1·62 at higher temps. [f] Calc. from Gutmann (*loc. cit.*) below 25°; the plot of specific volume against fluidity curves slightly. Lutschinsky (*loc. cit.*) gives $B = 7{\cdot}12 \times 10^{-2}$ ml. cP g.$^{-1}$. [g] Extrapolated from data by Sugden, Reed, and Wilkins (*loc. cit.*): Ramsay and Shields (*loc. cit.*) imply values of $\gamma = 34{\cdot}1$ and 19·3 dyne cm.$^{-1}$ at 1° and 118·5° with a temp. coefficient of $\gamma$ of 0·126 dyne cm.$^{-1}$ deg.$^{-1}$; $\omega = 683{\cdot}8$ at 1° and 434·2 at 118·5°; Eötvös constant $k = 2{\cdot}12_5$. [h] Ref. 2. [i] Extrapolated from data by Gutmann (*loc. cit.*). Other values are $\kappa_{25} = 1{\cdot}7 \times 10^{-6}$ (Walden, *Z. phys. Chem.*, 1903, **43**, 445) and $1 \times 10^{-6}$ ohm$^{-1}$ cm.$^{-1}$ (Payne, *J.*, 1953, 1052). [j] Refs. 5 and 6. [k] Ref. 7 and Lutschinsky and Likhacheva, *J. Phys. Chem. U.S.S.R.*, 1937, **9**, 65.

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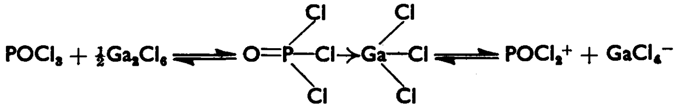
[8] McGowan, *Chem. and Ind.*, 1952, 495.

components. The kinematic and dynamic viscosities of the complex are also greater than the values for either component at their respective m. p.s and this effect is enhanced if all three compounds are compared at 118·5°; for example, the dynamic viscosity of the complex is twice that of gallium trichloride and nearly four times that of phosphorus oxychloride. Properties depending directly or indirectly on molar volume also increase on complex formation. These properties, which include the molar volume itself, $V_M$, Batschinski's constant $B$, the molar surface free energy $\omega$, and the parachor $[P]$ will be discussed more fully later.

Perhaps the most noticeable change during complex formation is the 1000-fold increase in electrical conductivity. This implies a great increase in the number of free ions and, as the activation energies of viscosity ($E_\eta$) and conduction ($E_\kappa$) are about the same, it is possible to use the reduced conductivity ($\mu\eta$) in these units to indicate the percentage degree of ionic dissociation.[9] The figures in Table 5 therefore suggest that, whereas the degree of ionic dissociation of molten gallium trichloride and liquid phosphorus oxychloride are both of the order of $10^{-4}$%, yet the corresponding value for the 1 : 1 complex is about ½%. The calculation should be correct to within a factor of 2 or 3. It is perhaps unnecessary to stress that conduction in the molten complex is not due to impurities, since the conductivity only appears when the two vacuum-distilled, non-conducting components are mixed, and its magnitude would require a concentration of several grams per litre of some fully ionised impurity such as potassium chloride. The degree of ionic dissociation of molten gallium trichloride–phosphorus oxychloride may be compared with the values obtained for certain co-ordination compounds of boron trifluoride:[9] the value of ½% is greater than the degree of dissociation of ester and ether complexes, about the same as that of boron trifluoride–triethylamine, and somewhat less than the values obtained for the alcohol complexes and hydrates. A rough comparison is also possible with molten gallium trichloride–benzoyl chloride[1] and molten stannic chloride–di(phosphorus oxychloride).[10] Thus, if one assumes that the density and viscosity of gallium trichloride–benzoyl chloride and gallium trichloride–phosphorus oxychloride are approximately the same, then the reduced conductivity of the benzoyl chloride complex, and hence its degree of ionic dissociation, is 0·3—0·4% which is very close to the value obtained for gallium trichloride–phosphorus oxychloride. The complex of stannic chloride with phosphorus oxychloride, however, seems to have a degree of dissociation which is less by a power of ten, as the published values of the specific conductivity and density imply a molar conductivity of $2{\cdot}5 \times 10^{-2}$ cm.$^2$ ohm$^{-1}$ and, if the viscosity is again taken as about 2 cP, then the reduced conductivity $\mu\eta$ is approximately 0·05. Only if the viscosity were as great as 15—20 cP would the estimated degree of ionic dissociation approach those of the gallium trichloride complexes discussed here.

The nature of the ionic species present in molten gallium trichloride–phosphorus oxychloride has not been established directly by the present investigation. There were no gaseous products of electrolysis. By analogy with the complex gallium trichloride–benzoyl chloride[1] the compound might be formulated as one in which a chlorine atom of phosphorus oxychloride was the electron donor, the compound so formed dissociating reversibly as dichloro-oxophosphonium tetrachlorogallate:



$$\mathrm{POCl_3} + \tfrac{1}{2}\mathrm{Ga_2Cl_6} \rightleftharpoons \mathrm{O{=}PCl_2{-}Cl{\rightarrow}GaCl_3} \rightleftharpoons \mathrm{POCl_2^+} + \mathrm{GaCl_4^-}$$

(0·0% at m. p.) (99·5%) (0·5%)

Such a scheme would be consistent with the transport measurements made on solutions of the related compound aluminium trichloride–phosphorus oxychloride which indicate

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[9] Greenwood and Martin, *J.*, 1953, 1427.

[10] Garner and Sugden, *J.*, 1929, 1298.

dissociation as $POCl_2^+AlCl_4^-$.[11] A test for this structure in the molten state might be obtained from chlorine-isotope exchange, but the more direct approach which is being followed is the investigation of the Raman spectrum of the solid and the melt. Similar experiments on saturated solutions of antimony pentachloride in phosphorus oxychloride have already been taken to indicate the presence of the ions $POCl_2^+$ and $SbCl_6^-$.[12] The alternative formulation of phosphorus oxychloride complexes in terms of electron donation by the oxygen atom, rather than by a chlorine atom,[10,13] is considered less satisfactory in view of the above arguments. Indirect evidence for the chlorine-donating structures is also afforded by the fact that, whereas phosphorus oxychloride forms an unstable addition compound with boron trichloride, it does not donate at all to the stronger electron-acceptor boron trifluoride.[14] This is difficult to interpret if oxygen is the donor atom, but is understandable if chlorine is the electron donor since the $BCl_4$ unit, though unstable, is nevertheless more stable than the unsymmetrical $BF_3Cl$ unit.[1]

The foregoing discussion has shown that, although gallium trichloride–phosphorus oxychloride is dissociated into ions to the extent of about ½%, the bulk of the molten phase comprises undissociated molecules or ion-pairs. It is therefore of interest to consider the volume change which occurs during complex formation. If two compounds in a condensed phase react to give an addition compound, one would expect a contraction in volume as a covalent, donor-acceptor bond between each pair of molecules is replacing the weaker van der Waals attraction : $D + A \longrightarrow D{:}A$. This contraction might be expected to be approximately the same for different systems and it is known that for complexes of boron trifluoride and for other donor-acceptor systems the decrease in molar volume is frequently about 10 ml.[15] For gallium trichloride–phosphorus oxychloride a contraction of 12·2 ml. mole$^{-1}$ is obtained on complex formation if this is measured at the m. p. of the complex (118·5°). The agreement with other donor–acceptor systems, however, may be fortuitous since, in this particular instance, the reaction is not one between monomeric donor and monomeric acceptor but one between monomeric donor and dimeric acceptor : $D + \frac{1}{2}A_2 \longrightarrow D{:}A$. The contraction might therefore be expected to be only half that observed for monomeric systems as only the ligand molecules become involved in extra bonding. Indeed, as the dimeric acceptor molecules have a bridge structure, two co-ordinate bonds are broken for each two formed, so that one might even imagine the reaction to occur with no change in volume. In fact, the volume change observed will depend on the temperature of comparison because the coefficients of expansion of the components and the complex are not the same. For example, if the comparison of molar volumes is carried out arbitrarily at the respective m. p.s of the various compounds, then Table 5 shows that complex formation involves an expansion of 4·6 ml. mole$^{-1}$ rather than a contraction.

Perhaps more significant is the change in value of Batschinski's constant $B$ which is obtained from the slope of the graph of specific volume against fluidity : $v = B\phi + b$ where $b$ is a constant. Batschinski's constant is related to the size of the flow units in the liquid so that the figures in Table 5 imply an increase in size of these kinetic units on complex formation. Rather different results would have been expected had the degree of ionic dissociation been considerably larger. The plot of specific volume against fluidity is also relevant to a discussion of the discontinuities which occur in the physical properties of supercooled liquids.[16] The present fluidity data for gallium trichloride–phosphorus oxychloride both above and below the m. p. can be represented by a single, slightly curved line, so that the small discontinuity observed in the Arrhenius plot of viscosity (Fig. 3) must be considered indecisive for this compound.

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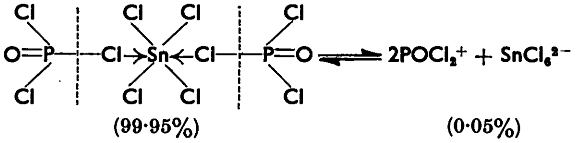
[11] Gutmann and Himml, *Z. phys. Chem.* (*Frankfurt*), 1955, **4**, 157.
[12] Maschka, Gutmann, and Sponer, *Monatsh.*, 1955, **86**, 52.
[13] Groeneveld, Proc. Symp. Co-ord. Chem., Copenhagen, 1953, 140; Payne, *ibid.*, p. 146.
[14] Burg and Ross, *J. Amer. Chem. Soc.*, 1943, **65**, 1637.
[15] Greenwood and Martin, *J.*, 1953, 4132.
[16] *Idem, Proc. Roy. Soc.*, 1952, *A*, **215**, 46.

The possible existence of the incongruently melting 2 : 1 compound gallium trichloride–di(phosphorus oxychloride) calls for brief comment. Such compounds of phosphorus oxychloride are well known but all may not have the same structure. Thus stannic chloride–di(phosphorus oxychloride) has been formulated as $(POCl_2^+)_2\,SnCl_6^{2-}$,[17] and even though the calculation presented above indicates that the degree of ionic dissociation is only of the order of 0·05%, the undissociated form can still be written in a way which implies electron donation from two chlorine atoms towards the central tin atom :



On the other hand gallium trichloride–di(phosphorus oxychloride) might merely be a solvate in which the second phosphorus oxychloride molecule is attached to the phosphorus atom rather than to the gallium :

$$POCl_3,POCl_2,Cl{\rightarrow}GaCl_3 \rightleftharpoons POCl_3,POCl_2^+ + GaCl_4^-$$

The alternative formulation involving five co-ordinate gallium seems less probable. A similar difficulty arises in the system of phosphorus oxychloride with titanium tetrachloride where two congruently melting compounds, $TiCl_4,POCl_3$ and $TiCl_4,2POCl_3$ have finally been established.[18] In other systems, such as those with zirconium and hafnium tetrachlorides, even the formulæ of the complexes formed are undecided and mole ratios $POCl_3 : MCl_4$ of 2 : 1, 1 : 1, 1 : 2, and 2 : 3 have been suggested.[19] It may well be that some of the supposed compounds are azeotropes rather than chemical individuals but there is clearly a need both for phase studies to establish the formulæ of the addition compounds and for electrochemical investigation to establish the degree of ionic dissociation of the complexes. Raman spectra or *X*-ray data could then be used to elucidate the structure of the groups so formed by deciding which atoms were involved in the donor–acceptor bonding.

[*Added, February* 11*th*, 1957.—The conductivity of $TiCl_4,2POCl_3$ at its m. p., 105°, has been reported as $1{\cdot}38 \times 10^{-3}$ ohm$^{-1}$ cm.$^{-1}$;[20] this corresponds to a molar conductivity of 0·384 ohm$^{-1}$ cm.$^{-1}$ and a reduced conductivity of about 0·75 if the viscosity is assumed to be 2 cP. The implied degree of ionisation, $\frac{3}{4}$%, is similar to that found for $GaCl_3,POCl$ but considerably larger than that of $SnCl_4,2POCl_3$. A phase study[21] of the system $ZrCl_4$–$POCl_3$ indicates two congruently melting compounds $ZrCl_4,POCl_3$, m. p. 205°, and $ZrCl_4,2POCl_3$, m. p. 184·7°, and this agrees well with cryoscopic results in nitrobenzene.[22] However, distillation gives a product which can be represented approximately as $3ZrCl_4,2POCl_3$.[23]]

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[17] Gutmann, *Z. anorg. Chem.*, 1952, **270**, 179.

[18] Groeneveld, van Spronsen, and Kouwenhoven, *Rec. Trav. chim.*, 1953, **72**, 950.

[19] van Arkel and de Boer, *Z. anorg. Chem.*, 1924, **141**, 289; Gruen and Katz, *J. Amer. Chem. Soc.*, 1949, **71**, 3843; Larsen, Howatson, Gammill, and Wittenberg, *ibid.*, 1952, **74**, 3489.

[20] Payne, *Rec. Trav. chim.*, 1956, **75**, 620.

[21] Sheka and Voitovich, *Zhur. neorg. Khim.*, 1956, **1**, 964.

[22] Larsen and Wittenberg, *J. Amer. Chem. Soc.*, 1955, **77**, 5850.

[23] Nisel'son and Ivanov-Emin, *Zhur. neorg. Khim.*, 1956, **1**, 1766.