27. *Studies of Valency. Part XV. The Dielectric Constants of Phosphorus Trichloride and Pentachloride.*

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IN a previous paper (Lowry and Jessop, J., 1930, 782), it was shown that sulphur tetrachloride exhibits the anomaly of having a higher dielectric constant in the solid state than when fused. This anomaly pointed to the occurrence of a change of molecular structure on fusion; it was therefore in harmony with observations which had already shown that the tetrachloride is decomposed to such an extent that it cannot be detected in the liquid state, except perhaps by its catalytic activity. The experimental observations were therefore interpreted by means of the equation

$$\underset{\text{Solid}}{[\overset{+}{S}Cl_3]\overset{-}{Cl}} \rightleftharpoons \underset{\text{Liquid}}{SCl_2 + Cl_2}$$

In the present paper similar observations are reported in reference to phosphorus pentachloride, where the dielectric constant falls on fusion to about two-thirds of its value in the solid state, *viz.*, from 4·23 at 22·8° to 2·85 at 160°. In this case, however, the fall of dielectric constant cannot be attributed to a complete dissociation of the higher chloride on fusion, since determinations of vapour density have shown that it persists to the extent of about 60% in the gaseous phase at 182° (Cahours, *Ann. Chim. Phys.*, 1847, **20**, 373). It appears likely, therefore, that the liquid contains integral molecules of PCl_5. These may be ionised to a limited extent in solution, perhaps according to the equation $PCl_5 \rightleftharpoons \overset{+}{P}Cl_4 + \overset{-}{Cl}$, since solutions of phosphorus pentachloride in nitrobenzene (Holroyd, *Chem. and Ind.*, 1923, **42**, 348) and of phosphorus pentachloride and pentabromide in liquid bromine (Plotnikov, *Z. physikal. Chem.*, 1904, **48**, 220; Plotnikov and Jakubson, *ibid.*, 1928, **138**, 235) are said to be conducting; but the extent to which the molecules are dissociated into ions in the molten pentachloride can only be very small, since the fused pentachloride and its solutions in phosphorus trichloride and in chlorine have only a minimal conductivity. The high dielectric constant of the solid, which is comparable with that of sylvine, must therefore be attributed to the separation of a polar modification which is only a minor component of the liquid; *e.g.*, the crystals may perhaps be an aggregate of ions of the type indicated above. This conclusion can only be established when the complex *X*-ray diagrams of the crystals have been analysed; but in the meanwhile independent evidence of the polar or salt-like character of the solid pentachloride is provided by its sparing solubility, not only in carbon tetrachloride, but also in liquid chlorine and in phosphorus trichloride, from which it is precipitated in much the same way as sulphur tetrachloride from sulphur dichloride and chlorine.

EXPERIMENTAL.

Methods.—The general method of measurement was similar to that used by Lowry and Jessop (*loc. cit.*). It was found, however, that the bank of small condensers, calibrated by a step method in terms of a small variable condenser, had sufficient mutual capacity to render this procedure inexact, since the change in capacity on disconnecting any one condenser was different according to which of its neighbours were also disconnected. Complete screening of each individual condenser is therefore essential. In the measurements now described, a single standard variable air condenser of capacity 70—180 μμF was used, after calibration to 0·02 μμF at the National

Physical Laboratory. In addition, the valve circuit was stabilised by substituting a high-tension accumulator, with a 2 μμF condenser in parallel, for the dry battery, and by wrapping the valve in cotton-wool.

Measurements with Phosphorus Trichloride.—The cell used for the experiments on the chlorides of sulphur was used again for measurements of the dielectric constant of phosphorus trichloride. It was calibrated with the following results :

Air		$\varepsilon = 1{\cdot}001$	$c = 13{\cdot}33$ μμF
Benzene	(16·3°)	$\varepsilon = 2{\cdot}289$*	$c = 25{\cdot}69$,,
Ether	(18·2°)	$\varepsilon = 4{\cdot}370$*	$c = 44{\cdot}67$,,

whence $c = 3{\cdot}401 + 10{\cdot}061\varepsilon - 0{\cdot}14127\varepsilon^2$

or $\varepsilon = 0{\cdot}3288 + 0{\cdot}097446c + 0{\cdot}00017235c^2$

* These values were selected by Hartshorn ("International Critica Tables," VI, 82).

The phosphorus trichloride was distilled from red phosphorus to remove any excess of chlorine, and fractionated through a column. The fraction boiling at 73·5° ± 0·2° was collected, and redistilled in a sealed apparatus by cooling the receiver with carbon dioxide and acetone. The distillate, which had been thus freed from the gaseous and solid products of hydrolysis, was transferred to the condenser by a similar method.

The dielectric constants of phosphorus trichloride over a range of temperatures were then determined, with a wave-length of about 250 metres, as follows :

Temperature. C.	Abs.	Density,† ρ.	c, μμF.	ϵ.	$P=\frac{\epsilon-1}{\epsilon+2}\cdot\frac{M}{\rho}$.	PT.	P (calc.).
17·0°	290·0°	1·5810	36·86	3·498	39·49	11,453	39·47
18·0	291·0	1·5792	36·78	3·490	39·42	11,470	39·44
33·3	306·3	1·5505	35·47	3·346	38·89	11,912	38·91
59·8	332·8	1·5000	33·58	3·139	38·13	12,690	38·11

† Guye and Baud, *Compt. rend.*, 1901, **132**, 1553.

The values of the dielectric constant are probably accurate to 2 in the last figure.

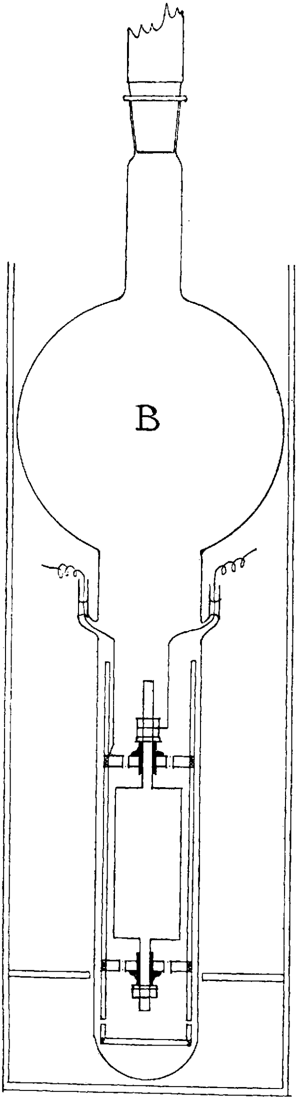
The calculated values of P were deduced from the equation $P = A + B/T$, where $A = 28{\cdot}90$, $B = 3066{\cdot}5$. This leads to a value of the electric moment :

$$\mu = 1{\cdot}272 \times 10^{-20}\sqrt{B} = 0{\cdot}70 \times 10^{-18} \text{ e.s.u.}$$

This is very similar to the value, $0{\cdot}80 \times 10^{-18}$, deduced by Bergman and Engel (*Physikal. Z.*, 1931, **32**, 507) for dilute solutions in carbon tetrachloride, thus indicating that the mutual influence of the molecules is not large. This conclusion is in harmony with the low boiling point of the liquid, in which there appears to be no extensive association.

Measurements with Phosphorus Pentachloride.—Although platinum electrodes are not readily attacked either by liquid chlorine or by phosphorus trichloride, they are attacked by mixtures of these two liquids. This action proceeds slowly at 65° and rapidly at 85°, so that on cooling from the latter temperature beautiful yellow crystals separated, in place of the usual white precipitate of the pentachloride. This yellow precipitate is probably identical with the compound, $2PCl_3,PtCl_2$ or $[Pt{\cdot}2PCl_3{\cdot}Cl_2]$, which was prepared by Schutzenberger and Fontaine in 1872 (*Bull. Soc. chim.*, **17**, 483) and examined again in 1903 by Rosenheim and Lowenstamm (*Z. anorg. Chem.*, **37**, 394).

FIG. 1.



Further experiments showed that silver was attacked, but that nickel, molybdenum, and tungsten were not affected, when heated with a mixture of phosphorus trichloride and pentachloride in a sealed tube at 180°, during a period of 48 hours; moreover, no nickel could be detected in the mixed chlorides by the dimethylglyoxime test. A condenser (Fig. 1) was therefore constructed of nickel, with Pyrex insulation and enclosed in a Pyrex vessel, through which tungsten leads were sealed. The capacity of the condenser was determined when filled with air (24·13 μμF), benzene at 18° (50·47 μμF), and phosphorus trichloride at 19·2° (72·26 μμF), giving the relation :

$$\varepsilon = -0{\cdot}006 + 0{\cdot}03846c + 0{\cdot}0001354c^2.$$

The pentachloride was introduced into the bulb *B* through a ground joint, and pumped out until nothing more could be condensed in a liquid-air trap except a little white solid pentachloride; the bulk of the solid had then also lost its yellow colour and its tendency to cohere. The bulb was sealed and heated until the pentachloride melted, ran down, and filled the condenser. The dielectric constants were then determined, in the liquid state and after solidification, as follows :

Liquid at 160°, $\varepsilon = 2{\cdot}85$.
Solid at 22·8°, $\varepsilon = 4{\cdot}23$.

The readings were less sharp than during calibration, since the resonance band was wide, perhaps by reason of a small electrolytic conductivity in the liquid; and bubbles of gas were liberated when the liquid crystallised as a white solid; but, since the apparatus had been exhausted, the normal volume of gas was probably negligible.

The numbers recorded above are rather higher than the preliminary values of Lowry and Jessop (*loc. cit.*, p. 790), *viz.*, $\varepsilon = 2{\cdot}7$ in the liquid at 165°, $\varepsilon = 4{\cdot}1$ in the solid at 130°, but they establish in a more precise form the anomaly which was then observed, and show that the high dielectric constant of the solid is not confined to the immediate neighbourhood of the freezing point, as in the cases studied by Errera (*Trans. Faraday Soc.*, 1928, **24**, 162).

Summary.

The dielectric constant of phosphorus trichloride falls from 3·498 at 17° to 3·139 at 59·8°. That of phosphorus pentachloride increases from 2·85 in the liquid at 160° to 4·23 in the solid at 22·8°. This increase is attributed to a change of molecular structure on crystallisation.

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