

5. The influence of pressure on the equilibrium constants can be attributed to deviations from the simple gas laws.

6. The true equilibrium constants for thermodynamical calculations have been determined by extrapolation to zero pressure. Calculations are given for  $\Delta F$ ,  $\Delta H$  and  $\Delta S$ .

7. The measurements indicate that the dissociations proceed according to the reactions  $N_2O_4 \rightleftharpoons 2NO_2$  and  $N_2O_3 \rightleftharpoons NO + NO_2$ .

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## THE DIELECTRIC PROPERTIES OF ANTIMONY PENTACHLORIDE AND PHOSPHORUS PENTACHLORIDE<sup>1</sup>

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The dielectric properties of antimony pentachloride and phosphorus pentachloride were studied in the hope of adding some information on which to consider the structure of these compounds.

The apparatus used has been described by Lowry and Jessop.<sup>2</sup> The materials used were carefully purified. The carbon tetrachloride was treated with chlorine and allowed to stand in sunlight for several days. It was dried with freshly fused calcium chloride and distilled. The antimony pentachloride was distilled three times in a vacuum and kept sealed in glass. It had a very light color and a sharp melting point. The phosphorus pentachloride used to make the solutions was contained in a small sealed glass vessel into which it had been distilled in vacuum.

In order to test out the apparatus, the dielectric constant of pure dry carbon tetrachloride was determined in it over a range of temperatures. These values and also the molar polarizations calculated from them are given in Table I. These agree very well with published data.<sup>3</sup> Pure benzene and chloroform were used to calibrate the cell. The densities

TABLE I

DIELECTRIC CONSTANT AND MOLAR POLARIZATION OF CARBON TETRACHLORIDE

Temp., °C.	Dielectric constant	Density, g./cc.	Molar polarization, cc.
3.5	2.268	1.62638	28.1
16.5	2.239	1.60128	28.1
26.3	2.217	1.58230	28.0
46.4	2.171	1.54264	28.0

<sup>1</sup> Part of this work was done during the time that one of the authors, J. H. Simons, was a National Research Council Fellow.

<sup>2</sup> Lowry and Jessop, *J. Chem. Soc.*, 782 (1930).

<sup>3</sup> Compare Stranathan, *Phys. Rev.*, 31, 653 (1928).

were determined with calibrated quartz floats by the method described by Lowry and Jessop.<sup>4</sup>

**The Molar Polarization of Antimony Pentachloride and Phosphorus Pentachloride in Solution in Carbon Tetrachloride.**—The density and capacity of these solutions were determined over a range of temperatures. The results are given in Tables II and III together with the molar polarizations calculated from them by means of the modified Clausius and Mosotti equation<sup>5</sup>

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{M_1 f_1 + M_2 f_2}{\rho} = P_1 f_1 + P_2 f_2$$

As the molar polarizations of both antimony pentachloride and phosphorus pentachloride show no appreciable deviation with temperature, it can be assumed that if these molecules have a dipole moment, it must be very small. Only a very dilute solution of phosphorus pentachloride could be made, as the solubility is low. The precision of the molar polarization calculated from the capacity of the solution is, therefore, not very high.

TABLE II

## MOLAR POLARIZATION OF ANTIMONY PENTACHLORIDE IN SOLUTION IN CARBON TETRACHLORIDE

Temp., °C.	Dielectric constant	Density, g./cc.	Molar polarization in cc.	
			Of solution	Of SbCl <sub>5</sub>
6.5	2.326	1.72191	30.1	47.6
14.0	2.313	1.70780	30.1	47.6
25.1	2.294	1.68592	30.2	48.5
40.4	2.267	1.65578	30.3	49.5
46.9	2.254	1.64260	30.3	49.5

Mole fraction of SbCl<sub>5</sub> . . . . . 0.105

TABLE III

## MOLAR POLARIZATION OF PHOSPHORUS PENTACHLORIDE IN SOLUTION IN CARBON TETRACHLORIDE

Temp., °C.	Dielectric constant	Density, g./cc.	Molar polarization in cc.	
			Of solution	Of PCl <sub>5</sub>
8.9	2.253	1.62638	28.2	33
21.9	2.226	1.60128	28.2	33
31.85	2.206	1.58230	28.2	33

Mole fraction of PCl<sub>5</sub> . . . . . 0.0311

**The Dielectric Constant of Antimony Pentachloride.**—This was determined over a range of temperature, the values being given in Table IV. The molar polarization was calculated from these measurements by means of the Clausius and Mosotti equation. This equation has been used previously for pure non-polar liquids, and so its use in this case is probably justified. These values agree well with those obtained from the capacity measurements of the carbon tetrachloride solution.

<sup>4</sup> Ref. 2, p. 1006.

<sup>5</sup> Debye, "Polar Molecules," The Chemical Catalog Co., New York, 1929, p. 45.

TABLE IV

DIELECTRIC CONSTANT	Temp., °C.	AND MOLAR Dielectric constant	POLARIZATION OF Density, g./cc.	ANTIMONY PENTACHLORIDE Molar polarization, cc.
	0.0	crystal	3.3	
	2.6	liquid	3.307	2.387
	17.6		3.220	2.356
	19.8		3.222	2.352
	20.9		3.212	2.349
	30.0		3.173	2.331
	38.4		3.136	2.314
	47.2		3.103	2.296
				54.1
				53.7
				53.8
				53.7
				53.5
				53.5
				53.4

**The Dielectric Constant and Conductivity of Phosphorus Pentachloride.**—The dielectric constant of phosphorus pentachloride was found to be as follows: crystal material at 135°, 4.2, and the liquid under pressure at 165°, 2.7. The conductivity of this compound was also measured with the following results

	Specific conductivity
Liquid at the melting point.....	6 × 10 <sup>-9</sup> reciprocal ohms
Crystal at 100°.....	3 × 10 <sup>-8</sup> reciprocal ohms
Crystal at 20°.....	3.3 × 10 <sup>-7</sup> reciprocal ohms

### Discussion

The dielectric constant of the crystalline phosphorus pentachloride being greater than for the liquid is a result that is both interesting and unusual. If we apply the method of Errera,<sup>6</sup> which uses the dielectric constant of the solid to determine  $P_0$ , in order to calculate the electric moment, we shall have negative values, for  $P - P_0$  will be negative. This makes the use of the method of Errera doubtful, for if it is certain that it cannot be used in this case, then its use in any other case is questionable.

A possible explanation for this result is that the crystal forces distort the molecule and increase the polarization, the molecule being symmetrical and without dipole moment in the liquid state. The conductivity measurements also indicate this, for the liquid has a lower conductivity than the crystalline material. The doubt that this casts upon the method of Errera is that molecules of other compounds may be more or less distorted when crystallized.

The zero or very small dipole moment of these compounds suggests a symmetrical structure. This is definitely in favor of a ten electron shell for the central atom with the five chlorine atoms attached by the five electron pairs. The polar formula,  $\text{SbCl}_4^+\text{Cl}^-$ , is definitely ruled out and grave doubts are cast on the structure advanced by Prideaux<sup>7</sup> in which three of the chlorine atoms are held by electron pairs and two held by single

<sup>6</sup> Debye, "Polar Molecules," p. 53.

<sup>7</sup> Prideaux, *Chem. & Ind.*, 42, 672 (1923).

electrons. Only one structure on this basis could give zero dipole moment and that one would have the three electron pairs in a plane with the two single electron bonds at right angles to this plane. Doubt is cast on this structure from three directions. The substance is diamagnetic, and it is difficult to see how two unpaired electrons on opposite sides of the central atom could neutralize each other's magnetic fields. The molecules dissociate readily to give the trichloride and chlorine, which may indicate that, if there are two chlorine atoms held differently than the other three, they should be adjacent. Chemical reactions such as the hydrolysis with water to form the oxychloride also indicate the same. The double molecule formula,  $\text{SbCl}_3 \cdot \text{Cl}_2$ , is ruled out by the vapor density measurements, which show  $\text{SbCl}_5$  to exist in the gas phase.

### Summary

The molar polarizations of antimony pentachloride and phosphorus pentachloride have been measured in carbon tetrachloride solutions and the dipole moments concluded to be either zero or very small.

The dielectric constants of antimony pentachloride and phosphorus pentachloride have been measured for both liquid and crystalline states.

The specific conductivity of phosphorus pentachloride has been measured.

Antimony pentachloride and phosphorus pentachloride are assumed to have a symmetrical structure with a ten electron shell for the central atom.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY SECTION, U. S. BUREAU OF MINES]

## THE ENTROPY AND FREE ENERGY OF METHANE<sup>1</sup>

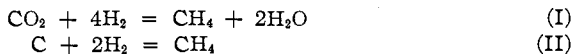
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### Introduction

In a recent publication<sup>3</sup> C. G. Maier reported a discrepancy of about five entropy units between the entropy of methane as calculated by way of low temperature specific heat data and the third law of thermodynamics, and that obtained from Randall and Gerard's<sup>4</sup> and Randall and Mohammad's<sup>5</sup> work on equilibria in the reactions



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<sup>3</sup> Maier, "Zinc Smelting from a Chemical and Thermodynamic Viewpoint," U. S. Bureau of Mines Bulletin 324 (1930).

<sup>4</sup> Randall and Gerard, *Ind. Eng. Chem.*, **20**, 1335 (1928).

<sup>5</sup> Randall and Mohammad, *ibid.*, **21**, 1048 (1929).