was greater at the higher temperatures because of slight improvements in apparatus and technique. The values are believed to be accurate within 2 to 3 parts per 1000.

Ipatiew and Teodorowich[8] measured the solubility of hydrogen in liquid ammonia at 25° and at pressures to 250 atmospheres. Their results are somewhat lower than ours over their whole pressure range.

Much additional information, some of which is now being secured, is needed before a thermodynamic treatment of the solubility of hydrogen in liquid ammonia can be given.

We wish to express our appreciation to Dr. C. H. Meyers for the generous assistance he has rendered in the course of the gage calibration.

Summary

The solubility of hydrogen in liquid ammonia was determined at 25, 50, 75 and 100° up to 1000 atmospheres total pressure.

The solubility (cc. of gas at S. T. P. per g. of ammonia) increases with temperature.

WASHINGTON, D. C. RECEIVED AUGUST 16, 1934

[8] V. V. Ipatiew and V. P. Teodorowich, *J. Gen. Chem.*, **2**, 305 (1932).

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA]

The Dielectric Behavior of Germanium Tetrachloride

BY JOHN G. MILLER

This paper presents a study of the dielectric properties of germanium tetrachloride as a liquid and in solution in carbon tetrachloride. The measurements indicate zero moment for this molecule while allowing very satisfactory calculation of its electronic and atomic polarizations.

Experimental Part

Apparatus.—Capacitance measurements were made by a bridge method at frequencies in the broadcast band. A General Radio 516-A bridge[1] was employed with a General Radio 484-A modulated oscillator as power supply. The null indicator was a commercial superheterodyne receiver having a sensitivity of 10 microvolts and shielded in a copper-lined box. The voltage applied to the bridge never exceeded 1 volt; the null point heard on the loud-speaker was very sharply defined, even at very low power being within the backlash of the standard precision condenser, which was a General Radio 222-M instrument. The condenser and resistance units of the balancing arm of the bridge were kept in series throughout, although the resistances used were always extremely small.

The measuring cell was of the type designed by Smyth and Morgan[2] and was supported in a glass tray. Leads to the standard condenser were of stout brass arranged to give a constant minimum of inductance and capacity with one another. The cell was thermostated in an oil-filled bath kept constant within 0.05° for the temperatures 15 to 55°, while at 0° an ice-water bath was used. The cell was calibrated from time to time using benzene and air.

The inductance and parasitic capacity of the measuring circuit in shunt with the standard condenser were found to be quite low. The former was approximately 0.6 microhenry, while the latter, made up of the lead, stray and fixed capacities amounted to less than 7% of the circuit capacity when the cell was filled with air. Rather than evaluate the inductance in this circuit to correct the capacitance determinations, it was found more convenient and reliable to measure capacitance over seven or eight frequencies covering the broadcast range and to extrapolate these readings to zero frequency where inductance error drops out. The curves obtained were quite similar among themselves and to those obtained by assuming a value for the inductance of the circuit, indicating greater accuracy and convenience in this extrapolation method since the small inductance would be difficult to evaluate and keep constant from one circuit setting to another. The apparatus and method were tested with carbon tetrachloride from 0 to 55° and the results were extremely satisfactory.

Densities were determined with a pycnometer similar to that used by Smyth and Morgan[2] and having a volume of 25 cc. It was thermostated in the baths used for the dielectric cell. Refractive indices were measured with a Pulfrich refractometer. The cell and prism were thermostated by water pumped through their jackets from a thermostat kept constant within 0.02°. The room temperature was kept within 1° of the temperature used (30°).

The pure liquids used in all measurements were distilled into each measuring cell by means of an all glass distillation apparatus ground to fit the refractometer and dielectric cells as well as the pycnometer. The important body of this apparatus is shown in Fig. 1 attached to the refractometer cell. The material was distilled through an all glass three-ball Snyder column which fitted the receiver at the ground joint A. Stopcock B permitted distillation at reduced pressure or at dry air pressure. The carefully ground mercury-seal stopcock C allowed removal of undesired fractions through D and entrance of the desired material into the apparatus through E which conveniently extended below the ground joint on the outer jacket F. This outer jacket was equipped with a two-way cock G

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[1] Burke, *General Radio Experimenter*, **7**, 1 (July, 1932).

[2] Smyth and Morgan, THIS JOURNAL, **50**, 1547 (1928).

which allowed filling the cell at dry air pressure or by suction. This apparatus was found to be very convenient in filling the cells, especially the pycnometer, and provided a great economy of materials.

In preparing the solutions the liquids were distilled in turn into a small weighing flask which was fitted with a glass stopper and kept in a desiccator between weighings and transfer of the solutions. The solutions were transferred to the apparatus by means of a well trapped suction arrangement.

Separate samples and independent measurements were used as checks throughout all the work. The agreements were always quite satisfactory.

Materials.—Germanium tetrachloride was prepared from 100-mesh germanite by decomposition with nitric acid, followed by digestion of the insoluble residue with concentrated hydrochloric acid and distillation. The product was washed with concentrated hydrochloric acid to remove arsenious chloride[3] after which it was again distilled and washed with hydrochloric acid. The resultant material was found free of arsenic and was placed in an all-glass apparatus where it was treated with sodium carbonate while dry air was passed through it. Next it was distilled through the eight-ball Snyder column of this apparatus. The material boiling at 83.0–83.8° was stored in small glass sealing bottles.

The benzene and carbon tetrachloride were Baker c. p. material and were distilled over sodium, the former being stored over sodium and the latter over calcium chloride.

Results and Discussion.—The polarization of germanium tetrachloride in carbon tetrachloride solution was measured over a wide range of concentrations at 30°. The mole fractions of the germanium tetrachloride c_2, the dielectric constants ϵ and the densities d, together with the polarizations of the solutions $P_{1,2}$ and those of the germanium tetrachloride P_2, appear in Table I. The value of the polarization of carbon tetrachloride was taken as 28.20.[4,5,6] The polarization of germanium tetrachloride in these solutions is substantially independent of concentration and has the same value as the pure liquid at the same temperature. This in itself suggests a lack of moment and indicates that study of the pure liquid should give the total polarization.

TABLE I

THE POLARIZATION OF GERMANIUM TETRACHLORIDE IN CARBON TETRACHLORIDE SOLUTION AT 30°

c_2	ϵ	d	$P_{1,2}$	P_2
0.0843	2.235	1.6015	28.94	36.99
.1393	2.251	1.6183	29.51	37.60
.2403	2.274	1.6490	30.44	37.52
.3893	2.301	1.6924	31.71	37.22
.5114	2.325	1.7271	32.78	37.12
.6917	2.360	1.7750	34.40	37.16
1.0000	2.417	1.8533	...	37.12

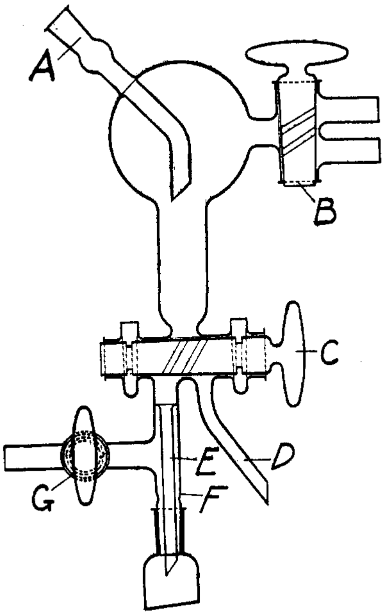

Fig. 1.

The dielectric constants, densities and total polarizations of pure liquid germanium tetrachloride measured from 0 to 55° appear in Table II. The slight increase of total polarization with increasing temperature is typical of non-polar liquids, being ascribed to the increase of the electronic polarization.[7,8] These measurements with the pure liquid and its solution in carbon tetrachloride show zero permanent moment for germanium tetrachloride, suggesting a symmetric tetragonal structure for the molecule in analogy to the results obtained by others[9,10,11,12] for the

TABLE II

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS OF GERMANIUM TETRACHLORIDE

Temp., °C.	ϵ	d	P
0	2.491	1.9226	37.03
15	2.455	1.8880	37.09
20	2.443	1.8762	37.12
25	2.430	1.8647	37.12
30	2.417	1.8533	37.12
35	2.407	1.8415	37.18
40	2.395	1.8296	37.20
45	2.383	1.8181	37.22
50	2.370	1.8063	37.22
55	2.360	1.7943	37.28

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(3) Allison and Müller, THIS JOURNAL, **54**, 2833 (1932).

(4) Williams and Krchma, *ibid.*, **49**, 1676 (1927).

(5) Stranathan, *Phys. Rev.*, **31**, 653 (1928).

(6) Morgan and Lowry, *J. Phys. Chem.*, **34**, 2417 (1930).

(7) Meyer, *Z. physik. Chem.*, **8B**, 42 (1930).

(8) Goss, *J. Chem. Soc.*, 1341 (1933).

(9) Williams, *Physik. Z.*, **29**, 174 (1928).

(10) Sänger, *ibid.*, **27**, 556 (1926).

(11) Bergmann and Engel, *Z. physik. Chem.*, **13B**, 232 (1931).

(12) Ulich, Hertel and Nespital, *ibid.*, **17B**, 369 (1932).

tetrachlorides of carbon, silicon, titanium and tin. Wierl[13] found a similar result for these tetrachlorides including that of germanium, in a study of electron diffraction.

The density values for the pure liquid agree very well with the few given in the literature[14] and in themselves give an excellent linear relationship with the temperature ($d = 1.9229 - 0.00233\ t$). The dielectric constant values agree very well among themselves although they are at variance with the rough value 2.65 determined at 30° by Lear[15] as the average of three rather discordant values: 2.60, 2.60, 2.75. The numerous checks applied in the present work allow us to discard Lear's value which has caused Ulich and Nespital[16] to estimate rather high values for the total and atomic polarizations of germanium tetrachloride.

Since the molecule has no orientation polarization, the atomic polarization P_A may be calculated by subtracting the electronic polarization P_E from the total polarization. To estimate the electronic polarization, molecular refraction MR was determined at 30° for the sodium D line and the hydrogen α, β and γ lines. The molecular refraction for infinite wave length MR_∞, *i. e.*, P_E, was obtained by use of the dispersion formula

$$MR_\infty = \left(1 - \frac{\lambda_0^2}{\lambda^2}\right)\left(\frac{n^2 - 1}{n^2 + 1}\frac{M}{d}\right)$$

where λ_0 is the wave length corresponding to a characteristic frequency of vibration in the ultraviolet, and λ is the wave length corresponding to the index of refraction n. The results appear in Table III. The value of P_E, 30.594, was obtained by solving simultaneous equations rather than by evaluating λ_0. The agreement of the six solutions of the equation was excellent and indicates an important vibration frequency corresponding to a wave length of 101.4 mμ.

TABLE III

INDEX OF REFRACTION AND MOLECULAR REFRACTIVITY OF GERMANIUM TETRACHLORIDE AT 30°

	n	MR
H_α	1.45417	31.342
Na_D	1.45730	31.528
H_β	1.46501	31.986
H_γ	1.47110	32.346

$MR_\infty = P_E = 30.594$

This value of P_E corresponds to a value of 6.53 for the atomic polarization of germanium tetrachloride at 30°, which places its value between those of titanium and tin in the fourth group series: carbon tetrachloride 3, titanium tetrachloride 5.7, tin tetrachloride 10.6.[12,16,17] Increasing size of the central atom in such a series and the accompanying decrease in binding force as revealed in the refractions seem to explain such an ordered rise in atomic polarization.[16,18,19]

The author intends to study the behavior of other halogenated germanes. Acknowledgment is made of a grant from the Faculty Research Committee of the University which aided in the purchase of equipment. The author is also indebted to Dr. C. E. Gulezian who aided in the preparation of the germanium tetrachloride.

Summary

1. Germanium tetrachloride has been shown to possess zero moment.

2. Values have been obtained for the electronic and atomic polarizations of germanium tetrachloride at 30°.

PHILADELPHIA, PENNA. RECEIVED AUGUST 17, 1934

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[13] Wierl, *Ann. Physik*, **8**, 521 (1931).

[14] Gmelin, "Handbuch der anorg. Chemie," 8 Aufl., Syst.-N. 45, Germanium, Verlag Chemie, G. m. b. H., Berlin, 1931, p. 42.

[15] Lear, *J. Phys. Chem.*, **28**, 888 (1924).

[16] Ulich and Nespital, *Z. Elektrochem.*, **37**, 559 (1931).

[17] Errera, "Polarisation Diélectrique," Les Presses Universitaires de France, Paris, 1928, p. 100.

[18] Smyth, THIS JOURNAL, **51**, 2051 (1929).

[19] Klemm and Henkel, *Z. anorg. allgem. Chem.*, **213**, 115 (1933).