Studies on Fluorine at Low Temperatures. VII. Determination of Dielectric Constants of Condensed Gases.

By Eizo KANDA.

(Received August 12th, 1937.)

The author set about determining the dielectric constants of condensed gases as a means of studying the state of their molecules. This paper deals with the determination of the dielectric constants of liquid oxygen, fluorine, chlorine, and hydrogen chloride.

I. Method and Apparatus. (1) *Electric circuit for determining the dielectric constant.* The electric capacity was determined by the "beat method". As this method is now extensively used and is well known, its essential points alone are given in the circuit diagram of Fig. 1. In Fig. 1, I is a variable frequency oscillator circuit comprising a cell C_x to be subjected to measurement and a variable condenser of high precision C_v (capacity, 1500 $\mu\mu$F) which is arranged parallel with C_x. III is a fixed frequency (10^6C.) oscillator circuit comprising a quartz-oscillator. The beat between I and III (1000 cycles) is amplified and detected by means of II which is loosely coupled with I and III. The sound is received by a loud speaker. The whole apparatus is kept in a copper case that it may be protected from external disturbances.

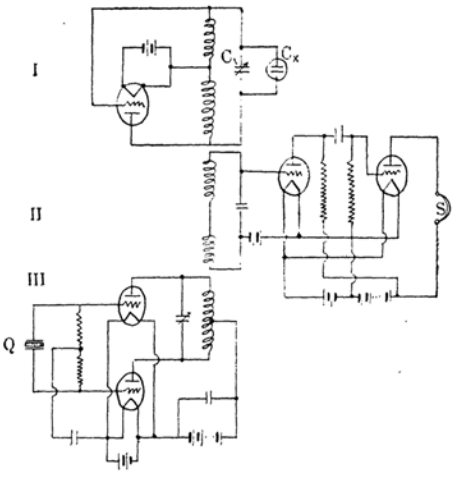

Fig. 1.

(2) *Cell.* (See Fig. 2, C) The cell consists of brass cylinders 90 mm. long and 1 mm. thick which are concentrically put one in another between the walls of a double-walled glass cylinder 39 mm. in outside diameter and 23 mm. in inside diameter. Some difficulties were encountered in working the glass so as to make it stand the low temperature. With such a device the temperature of the sample therein could be made uniform and a small amount of the sample was enough for the purpose.

Further, the cell-electrodes were gold-plated for fear of any great error being caused by a dielectric film which might have been formed on their surfaces by the action of fluorine or chlorine. Care was taken not to use them continuously for a long time. The cell had four long glass tubes for introducing lead wires and for taking in and out the sample. A quartz film pressure gauge was attached to one of the tubes. A platinum resistance thermometer R occupies the space in the centre of the cell. The capacity of the cell in the vacuous state was about 70 $\mu\mu$F.

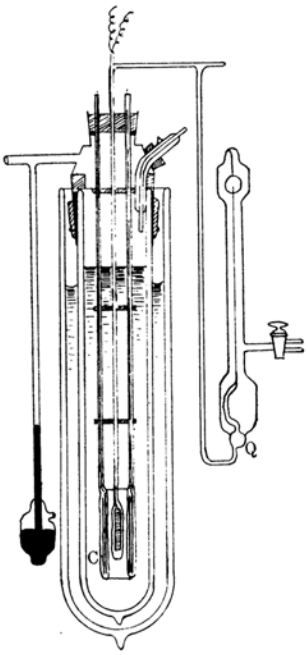

Fig. 2.

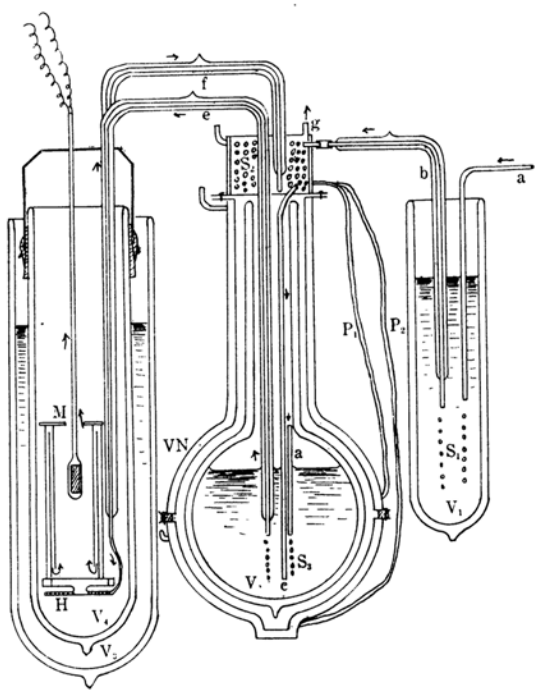

Fig. 3.

(3) *Cooling device.* Liquid nitrogen or liquid hydrogen was used for condensing the sample and for keeping the cell at a constant temperature. For keeping a constant low temperature, different devices were used according to the range of temperature of the measurement. Thus five kinds were used, which were (a) for 0° to −130°C., a device for automatically keeping a constant temperature, with pentane as the vessel liquid and indirectly cooled by liquid nitrogen, (b) for −130° to −183°C., a cryostat with vapour of liquid nitrogen as the cooling medium, (c) for −183° to −195°C., a cryostat using liquid oxygen and liquid nitrogen,

(d) for −195° to −250°C., a cryostat with vapour of liquid hydrogen as the cooling medium, (e) for −252° to −258°C., a cryostat using liquid hydrogen and solid hydrogen.

Of these, (a) and (c) have often been used in the author's experiments, and (e) is one which was used in the measurement of the specific heat of solid fluorine[1] and is outlined in Fig. 2. (b) and (d) were used for the first time.

Cryostat using hydrogen vapour. The apparatus illustrated in Fig. 3 was devised by consulting Leiden's[2]. V_1 is a Dewar vessel for liquid nitrogen, V_2 a Dewar vessel for storing and vaporizing liquid hydrogen, V_4 a cryostat containing hydrogen vapour, and V_3 a Dewar vessel containing liquid nitrogen and intended for reducing thermal conduction to V_4. Outside V_2 there is a double-walled jar V_N made of copper plate. Through the pipes P_1 and P_2 liquid nitrogen and its vapour are introduced between the walls of the jar for keeping the wall of V_2 at a low temperature. It is difficult to store liquid hydrogen for a long time on account of its very low temperature and its heat of vaporization per unit volume being very small as compared with that of liquid air (about 1/7). When V_2 was not protected by V_N, 4 litres of liquid hydrogen was vaporized in about 12 hours. When it was surrounded by V_N and kept at a low temperature with liquid nitrogen, it remained for about 18 hours.

The hydrogen gas enters at a and is cooled by the liquid nitrogen and liquid hydrogen vapour as it goes through S_1, b and S_2, and gets out in bubbles by C at the bottom of V_2. At the same time the liquid hydrogen in V_2 is vaporized. The vapour, starting from d, passes through S_3 and e and enters the spiral H near the bottom of V_4. There is a heating coil outside H, by which the temperature of the hydrogen vapour in H is adjusted. Thus the vapour goes up and down through the spacings in the triple wall of the copper cylinder over H, and finally enters the cylinder. This cylinder, intended for ensuring a uniform temperature, has a resistance thermometer. By controlling the flow of hydrogen gas and the heating of H, the temperature is adjusted. The hydrogen gas goes out by an opening in the upper part of M, and passes through the double-walled pipe f, and cooling the group of spirals S_2, gets out by g.

With this apparatus, any temperature between −195°C. and −250°C. could be kept constant with a variation of not more than 0.05°.

(4) *Determination of the density of condensed liquids.* For obtaining the molecular polarization of a liquid by measuring its dielectric con-

(1) See the eighth paper of this series.

(2) Onnes and Crommelin, *Commun. Phys. Lab. Univ. Leiden*, **No. 154C** (1921).

stant the density of the liquid must be determined. For this purpose an apparatus as shown in Fig. 4 was used. The whole apparatus was made of thin Pyrex glass. The volume of the capillary tube was accurately determined in advance. The test liquid was condensed in the capillary tube. The neck in the upper part of the apparatus was sealed by fusion. The temperature of the capillary tube was varied and the height of the liquid was measured by means of a comparator or cathetometer. Then the whole apparatus was brought to an ordinary temperature and the liquid was vaporized in the spherical part. Thus the weight of the sample was determined.

Table 1.

$T_{abs.}$	ρ (specific weight)	ε	P_M
87.62	1.158	1.487	3.856
78.20	1.202	1.511	3.872
68.00	1.250	1.538	3.891
59.51	1.290	1.556	3.882

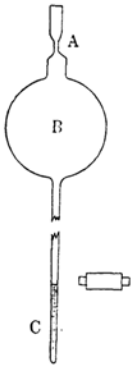

Fig. 4.

II. **Results of the Measurements.** (1) *Liquid oxygen.* See Table 1. The error of the dielectric constant was in a range of ±0.1%.

The molecular polarization of oxygen could be regarded as almost independent of the temperature. Thus, m (molecular moment of liquid oxygen) = 0 could naturally be expected.

(2) *Liquid fluorine.* See Table 2. Table 2 also shows that there was no regular variation in P_M. The irregular variation was considered due to the error of measurement. Therefore the molecular moment is zero.

(3) *Liquid chlorine.* Commercial liquid chlorine, after subjected to five fractional distillations, was used (Table 3).

According to Lewis,[3] liquid chlorine also has a very small moment, which, however, could not be ascertained from the above P_M. The author

(3) Lewis, "Valence and the Structure of Atoms and Molecules"; C. Smyth, *J. Am. Chem. Soc.*, **46** (1924), 2151.

Table 2.

$T_{abs.}$	ρ	ε	P_M
57.40	1.204	1.567	5.012
60.51	1.195	1.561	5.008
64.41	1.185	1.553	4.989
68.38	1.154	1.546	5.069
73.00	1.141	1.536	5.046
75.01	1.136	1.533	5.100
79.40	1.124	1.524	5.024
83.21	1.113	1.517	5.016

Table 3.

$T_{abs.}$	ρ	ε	P_M
208.00	1.643	2.147	11.94
210.51	1.636	2.139	11.93
215.60	1.621	2.123	11.92
220.61	1.605	2.104	11.90
227.90	1.580	2.088	11.95
235.50	1.555	2.059	11.90
239.96	1.530	2.048	12.00

intends to make further determination of the dielectric constant with a dilute solution.

(4) *Hydrogen chloride.* Hydrogen chloride was prepared by dropping concentrated sulphuric acid on sodium chloride and warming of the mixture. The gas thus produced was washed with sulphuric acid. After dried with phosphorus pentoxide, the gas was liquefied and refined by repeated fractional distillation. The liquid boiled at 168°K. and freezed at 159°K.

Table 4.

$T_{abs.}$	ρ	ε	P_M
160.01	1.267	11.80	22.55
163.25	1.258	11.42	22 52
165.60	1.251	11.16	22.52
168.11	1.244	10.85	22.49
170.25	1.239	10.60	22.44
173.50	1.230	10.21	22.38
176.75	1.221	9.84	22.32
178.00	1.218	9.70	22.28
181 15	1.211	9.31	21.99
182.76	1.206	9.12	22.15

Table 5.

$T_{abs.}$	ε
101.50	11.01
106.82	11.21
112.50	11.42
121.75	11.76
130.05	12.23
136.90	12.68
140.35	13.06
149.21	13.12
153.50	13.06
99	Transition point
98.5	3.10

P_M (Table 4) clearly showed a tendency to decrease with the rise of temperature. It may be said to have a great moment. Measurements with liquid hydrogen chloride at three points between 158°K. and 165°K.

were made by Cone[4] and by Smyth,[5] but, as the ranges of temperature of their measurements were very small and the number of points of measurements also very small, no such tendency was seen in their experiments.

Measurement was also carried out with solid hydrogen chloride, Table 5. ε had at first a tendency to increase with the fall of temperature as was the case with liquid hydrogen chloride. However, this was the reverse of the tendency of normal solids. The fact shows that hydrogen chloride does not immediately form perfect crystals even when it is brought to a temperature below the freezing point, but that it ceases innermolecular rotation and makes perfect crystals only when it reaches the next transition point (99°K.).

P_M was not calculated because the density of the solid was not clear.

It will be interesting to make a study of the change in the molecular heat, especially in the electric field with reference to the result of the study on the dielectric constant, of hydrogen chloride making "Rotationsumwandlung" and of other hydrogen halides, ammonium halides, and others making similar transition.[6]

The results of measurements with O_2, F_2, Cl_2, and HCl are illustrated in Figs. 5 to 8.

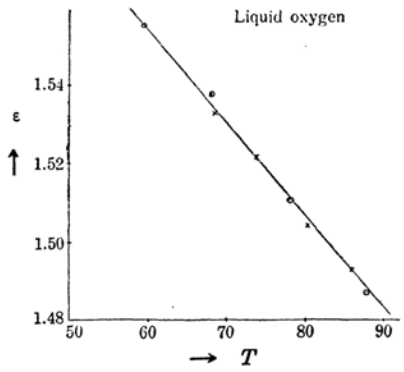

Fig. 5.

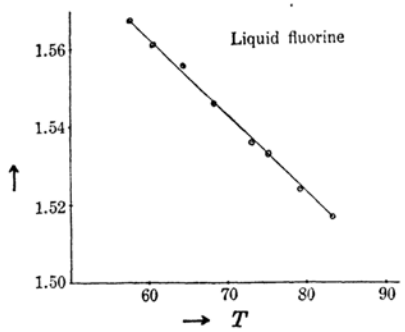

Fig. 6.

⊙ Kanda × Werner and Onnes[7]

(4) Cone, *J. Am. Chem. Soc.*, **53** (1931), 1278.

(5) Smyth, *J. Am. Chem. Soc.*, **55** (1933), 1830.

(6) Pauling, *Phys. Rev.*, **36** (1930), 480; Fowler, *Proc. Roy. Soc.* (London), A, **149** (1935), 1.

(7) Werner and Onnes, *Commun. Phys. Lab. Univ. Leiden*, **No. 178C** (1926).

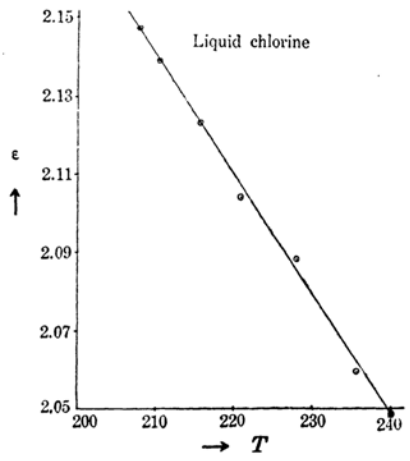

Fig. 7.

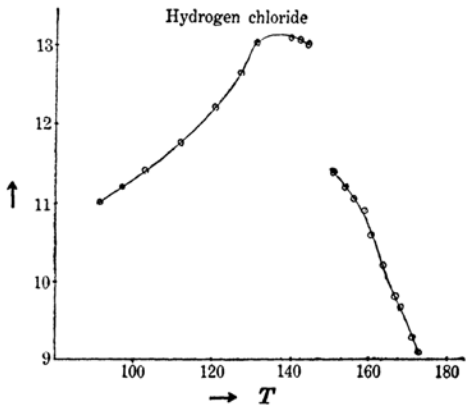

Fig. 8.

The author expresses his cordial thanks to Prof. Aoyama under whose guidance the present work was carried out and thanks are due to Prof. Mizushima of the Tokyo Imperial University, who kindly advised him through the investigation. He is also very much indebted to the Japan Society for the Promotion of Scientific Research for a grant.

Cryogenic Section,
Research Institute for Iron, Steel and Other Metals,
Tohoku Imperial University.