Physics. — *"Preliminary measurements of the dielectric constants of liquid and solid nitrogen."* By L. EBERT and W. H. KEESOM. (Communication N°. 182*d* from the Physical Laboratory at Leyden).

(Communicated at the meeting of September 25, 1926).

§ 1. The dielectric constants of liquid and solid nitrogen have not previously been measured. In this communication some preliminary measurements will be published. The departure of one of us is the motive for communicating these measurements, which cannot yet be considered as definite.

§ 2. *Apparatus and corrections.* The apparatus used was the same as that used for the measurements on liquid oxygen by WERNER and KEESOM[1]). We always used condenser *B* (l.c. § 2). Since the existence region of liquid nitrogen is situated wholly within that of liquid oxygen, for measurements on liquid nitrogen the cryostat could always be filled with liquid oxygen. On one occasion we succeeded in obtaining solid nitrogen in the condenser, and in taking measurements on it.

The temperature exchange took place each time with satisfactory rapidity.

The accuracy in these measurements is not so great as in those with liquid oxygen (l.c. § 5), chiefly for the following two reasons.

In the first place we did not succeed in establishing that, after a series of measurements (this is after the apparatus had been cooled to $-200°$ C. for 24 hours or longer) the capacity of the condenser empty returned to the same value, which it had at the beginning of the measurements. As an example, in table I, two measurements are given, which are done with particular care, in order to investigate whether the geometric capacity is reproducible. Probably this effect is due to a thermic deformation, adjusting itself very slowly. Now it is difficult to establish, which zero-value of the capacity must be taken into account for each moment of a series of measurements. This uncertainty of the zero-value (5 à 7 $^0/_{00}$) surpasses that of each capacity measurement by one order of magnitude.

In the second place it is not easy to see, how large the correction for the capacity of the leading wires must be chosen in each single case. The principal thing here is the condenser consisting of the wire *D* and the metal tube *H*. The question whether the tube *H* is totally

[1]) These Proceedings **29**, 306, 1926; Comm. Leyden N°. 178c.

TABLE I.

Geometric capacity of the condenser before and after a series of measurements [1].			
Date	Time	Temperature	Capacity in arbitrary units [2]
Jan. 18.26	11h a.m.	— 183° C.	32.76 ± 0.01
„ 19.26	3h p.m.	— 183	32.95 ± 0.01
May 6.26	10h a.m.	— 195	30.70 ± 0.008
„ 7.26	10h p.m.	— 195	30.97 ± 0.003

filled with the liquid to be investigated or not is then of great importance. In the first case the correction to ε is very small ($< 1\ ^0/_{00}$), in the second case it rises above $1\ ^0/_0$. The condenser was filled with nitrogen by condensation of the gas under 1 atm. overpressure, the pressure of the oxygen in the cryostat being sufficiently reduced. Filling of the cryostat with nitrogen was always continued for a long time after the liquid surface had disappeared behind the lower rim of the cap C, but for these measurements it was not possible to say to what height in H the liquid stood in each single case. Particular attention must be paid to the fact that the contraction of liquid nitrogen between boiling point and melting point amounts to $8\ ^0/_0$, so that the level of the surface in the upper, relatively narrow part of the apparatus may have fallen greatly during the course of a series of measurements. In what follows calculations were always made as if H was quite full. The correction for this not being so would *increase* the value of ε.

The temperature of the condenser was measured with the aid of the platinum thermometer T (l. c. fig. 1).

The nitrogen was taken from a cylinder, the contents of which appeared to contain according to an analysis about $3\ ^0/_{00}$ oxygen. Before the condensation the nitrogen was led through a moisture trap which was cooled with liquid air.

That the nitrogen was indeed very pure follows also from the value, which was derived from the point of retardation in the cooling curve for the freezing point, namely 63.14° K. ± 0.1°, while EUCKEN [3]) obtained for it 63.19, KEESOM and KAMERLINGH ONNES [4]) 63.06, CATH [5]) 63.23.

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[1]) Each time at the same temperature, etc.

[2]) For each number the probable error is indicated of the average derived from 5 to 10 readings.

[3]) A. EUCKEN, Verh. d. D. physik. Ges. **18**, 4, 1916.

[4]) These Proceedings **18**, 1247, 1916; Comm. Leyden N°. 149*a*.

[5]) These Proceedings **21**, 656, 1918; Comm. Leyden N°. 152*d*.

§ 3. *The results.* During the preparations for the measurements several unexpected disturbances appeared, which took considerable time to overcome. Owing to this the number of measurements, which can be considered as trustworthy, is small. Table II gives the results of these measurements.

TABLE II.

Dielectric constant of liquid nitrogen.

Date	Temperature T (°K.)	Capacity		D. C.		Density ϱ	Molec. polarisation	
		C_0	C	ε_1	ε_2		P_1	P_2
Jan. 18.26	90.0	32.76	—	—	—	—	—	—
	66.7	—	47.95	1.464	(1.453)	0.8540	4.389	(4.305)
	63.9	—	48.21	1.472	(1.461)	0.8653	4.398	(4.310)
„ 19.26	76.5$_4$	—	47.51	(1.451)	1.440	0.8108	(4.446)	4.351
	90.0	32.95	—	—	—	—	—	—
May 6.26	78.0	30.70	—	—	—	—	—	—
	74.8	—	44.52	1.451	1.438	0.8185	4.471	4.358
„ 7.26	78.0	30.97	—	—	—	—	—	—

Regarding the separate columns of this table, the following remarks may be made.

In the two series of measurements C_0 is different owing to a thorough cleaning of the interior of the condenser and to several small repairs, which took place meanwhile.

ϱ has been interpolated from the measurements of MATHIAS, KAMERLINGH ONNES and CROMMELIN [1]); P indicates the expression $\frac{\varepsilon-1}{\varepsilon+2}\cdot\frac{M}{\varrho}$.

The columns ε_1, P_1 contain the values, calculated with the zero capacity *before*, ε_2, P_2 those, calculated with the zero capacity *after* the experiment.

If one of the two numbers stands between ( ), then there is a large time-interval between the measurement and the zero capacity used, in this case probably the value not placed between ( ) is preferable.

On Jan. 18, it was possible sufficiently to regulate the temperature of the cryostat for oxygen pressures of 7.6 and 5 mm respectively. So we could obtain some very preliminary values for solid nitrogen; see table III.

[1]) These Proceedings **17**, 953, 1914; Comm. Leyden N^0. 145c.

TABLE III.

Dielectric constant of solid nitrogen.				
Date	Temperature	Capacity	ε_1	ε_2
Jan. 18.26	61.9° K.	48.12	1.469	1.458
	59.9	47.90	1.462	1.452

Here we do not know ϱ, so P cannot be calculated.

§ 4. *Discussion. a.* Liquid nitrogen.

The mean of the values P not placed between ( ) from table II is 4.39. For comparison the following values can serve.

1. $\frac{n^2-1}{n^2+2} \cdot \frac{M}{\varrho}$ for liquid nitrogen at $T = 77.1°$ K. From data of GEROLD [1]) follows by extrapolation for $\lambda = \infty$: $n = 1.1983$; ϱ is 0.8082 (see above). Then

$$R_{liq} = \frac{n^2-1}{n^2+2} \cdot \frac{M}{\varrho} = 4.396.$$

2. The same expression for gaseous nitrogen at 77.97° K. and 752.3 mm. pressure. From the data of GEROLD (l.c. p. 88) follows $\varrho = 0.004556$ (recalculated after BOYLE-GAY-LUSSAC). For n_∞ 1.001073 was chosen. Then

$$R_{gas} = 4.395.$$

3. The same expression for gaseous oxygen under normal circumstances gives n_∞ being 1.000295:

$$R_{gas} = 4.404.$$

4. The expression $P_{gas} = \frac{\varepsilon-1}{\varepsilon+2} \cdot \frac{M}{\varrho}$ for gaseous nitrogen under normal circumstances is not quite certain as the values given by various investigators are somewhat different. Recent, very careful measurements of ZAHN [2]) gave $\varepsilon = 1.000581$, the lowest value, obtained till now. From this follows:

$$P_{gas} = 4.34.$$

One can draw the conclusion, that the relation of MAXWELL as well as the equation of CLAUSIUS-MOSOTTI are approximately valid for

[1]) E. GEROLD, Ann. d. Phys. (4) **65**, 93, 1921.

[2]) CH. TH. ZAHN, Phys. Rev. **24**, 400, 1924.

gaseous and liquid nitrogen [1]). Our measurements give no data regarding the question whether it is necessary to change the formula of CLAUSIUS-MOSOTTI into the more universal formula $\frac{\varepsilon - 1}{\varepsilon + u} \cdot \frac{M}{\varrho}$ (as WIENER [2]) pleads), as this question is only to be answered by means of very accurate measurements. That the number ("form number") u should differ much from 2, seems however not probable because of the approximate validity of the equation of CLAUSIUS-MOSOTTI.

Further it should be remembered, that the validity of the rule of MAXWELL speaks against the existence of an appreciable dipole-moment and of an absorption, situated in the near infra-red.

b. Solid nitrogen.

In this case the meaning of the numbers is much less clear, because the density is not known. The values of ε are smaller than the values which would be valid for liquid nitrogen at the same temperatures. It is very possible, that this only appears to be so, and that those small values are only the result of the appearance of hollows in the solid dielectricum or of the crystals being more or less directed, by which an anisotropic dielectricum may be formed. These question could only be answered by a special investigation. If the values, obtained for solid nitrogen were valid for complete and isotropic filling, then the relation of CLAUSIUS-MOSOTTI could only hold for the change liquid → solid, if the density of solid nitrogen were smaller than that of liquid nitrogen.

One of us (E.) wishes also to express his thanks to the International Education Board, for granting a stipendium, which made a sojourn in the Physical Laboratory at Leyden possible for him.

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[1]) Be it remarked that the measurements of ZAHN for oxygen under normal circumstances give for $\frac{\varepsilon-1}{\varepsilon+2} \cdot \frac{M}{\rho}$ the value 0.1209 (see however the values of FRITS, Comm. Leyden N°. 178c, p. 33, note 1). This value agrees practically with the value 0.1211, which WERNER and KEESOM have obtained for the greater part of the existence region of liquid oxygen.

[2]) O. WIENER, Ber. d. Math. Phys. Kl. d. Kgl. Sächs. Ges. d. Wiss. **62**, 256, 1910; Abh. d. Math. phys. Kl. etc. **32**, N°. 6, 509, 1912; E. GEROLD, l.c., p. 94.