THE DIELECTRIC CONSTANT OF

LIQUID AMMONIA.

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The determination of the dielectric constant of liquid ammonia over the temperatures ranging from its boil-point,- 33.5° C, to its critical temperature, 131° C, was begun by Mr. W. H. Rodebush.+ Measurements were made up to 80 C. The object of this research was to check the results obtained by Mr. Rodebush and, if possible, to carry the measurements on up to the critical temperature of ammonia.

The work has been carried on under the direction of Dr. Cady and is a part of the work which he is directing upon liquid ammonia to determine if there is any relation between the degree of dissociation of a salt in an electrolyte and the dielectric constant of the electrolyte itself. Nernst ++ was one of the first to point out that the dissociation of a salt in a liquid must be due to the resultant action of two forces: first, a repelling force between the two ions, of whose nature we know nothing; second, the attractive force between the unlike charges of electricity on the two ions.

\+ W. H. Rodebush, Thesis, University of Kansas, 1914.

++ Zeit. für Phys. Chem., 13, 531, 1894.

This latter force should be represented by the formula,

$$f = ee'/Kd^2$$

where ee' are the charges of electricity, of opposite sign, upon the ions, d the distance between them and K the specific inductive capacity of the medium. Thus the higher the dielectric constant of an electrolyte the greater should be its dissociating power.

Many examples are at hand to show that as a general rule this is true. It is not possible, however, to trace any definite relationship between the dielectric constant of a liquid and its power of dissociation, due probably to other factors which vary from solvent to solvent. If, however, we could compare the change of dissociation of some salt in a solvent with the change of the dielectric constant of that solvent over a considerable range of temperature, we should be able to observe any relationship which existed between the two. It was with this purpose in view that the work was begun upon liquid ammonia. This liquid was chosen because it has far less solvent power upon glass and other containing vessels than water and can, therefore, be kept in a comparatively pure state when heated up under pressure in a containing vessel.

The principle employed in measuring the dielectric

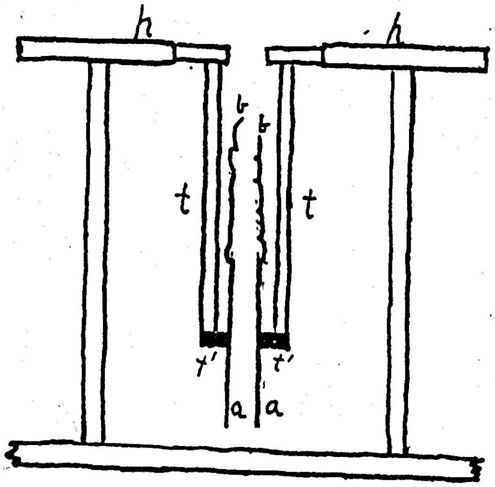


Fig. III.
1/10 natural size

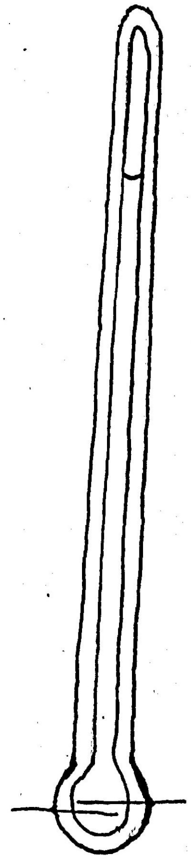


Fig II.
natural size

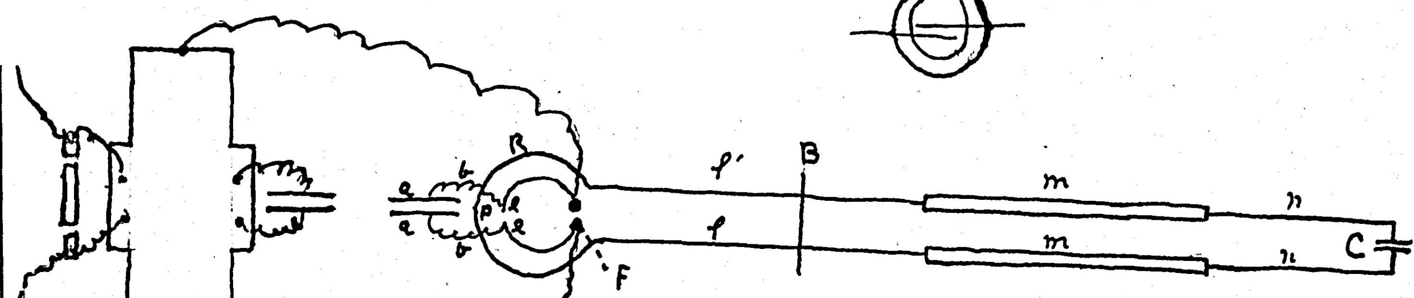


Fig. I

constant of the liquid ammonia was that devised by Lecher[+] using electric oscillation of high frequency. Lecher found the length of the parallel wires, BC, fig. 1, which, together with a condenser, C, form a circuit in syntony with a given source of oscillations. When a tube, A, containing a rarefied gas is laid across the wires it glows, unless the conducting bridge, B, is laid upon the wires. It then ceases to glow, but for one particular distance, the wires and the condenser form a circuit which is in resonance with the given oscillations, and the tube again glows. A wave traveling down two parallel wires may be considered as the motion of Faraday tubes of force down the wires; the ends of the tubes being considered as confined to the wires. The length of the circuit BC must, then, be such that a series of Faraday tubes will travel down the parallel wires of the circuit, be reflected at C with a change of direction of the electric intensity and get back to B in time to reinforce the next wave of like sign that starts down the parallel wires. The result at resonance is a condition of steady oscillation analogous to sound waves in a pipe or waves in strings.

The reflection of the waves at C is a function of the capacity of the condenser and is given by the expression,[++]

$$\cot \frac{2\pi L}{\lambda} = C$$

+ Wied. Ann. 42, p. 142, 1891.

++ Ann. der Phys. u Chem., 61, 479, 1897.

Where L is the distance, BC, and is the wave length of two times the distance for resonance determined by replacing the condenser with a wire of neglible resistance.

Now since part of the lines of the condenser pass through the liquid dielectric, part through the glass, and part through the air, the capacity will be of the form

$$C = C^{\circ} + K_g C_g + K C'$$

If L is the distance BC when the condenser is filled with the unknown dielectric K, and L' the distance when filled with air, then K can be calculated from the expression

$$\cot \frac{2\pi L'}{\lambda} - \cot \frac{2\pi L}{\lambda} = 1-K$$

In practice it was found more satisfactory to calibrate the condenser by filling the condenser with liquids of known dielectric constants and plotting the known K's against the L's obtained. By measuring the L for the condenser filled with liquid ammonia the value of K for ammonia could then be read from the curve.

An outline of the apparatus appears in fig. 1. The general method is that of Drude:+ The electric oscillations are set up by the inductive method of Blondlot++.

\+ Ann. der Phys. u Chem. 61, 467, 1897.

++ Journal de Phys. ser. 2, vol. X, p. 549.

e e' are two semicircles of copper wire, 2mm in diameter, which form a circle about 5 cm. in diameter. The rear ends of these semicircles are separated by a gap of 4 mm. The front ends terminate in brass balls which form a spark gap of about 1 mm. length. e e, together with the loop of wire which surrounds them, are immersed in a vessel of kerosene oil to prevent sparks from jumping across and to prevent the rapid oxidation of the spark balls. The spark balls ff are connected to the terminals of the secondary of a Tesla coil. The secondary of this coil consists of about 15o turns of 1 mm. insulated copper wire wound on a glass cylinder. The primary of the coil consists of two wires of about 2 mm. diameter each of which is wound two and one-half times around the secondary but in opposite directions, and separated from the coils of the secondary by a space of about 1 cm. The whole coil is immersed in a light petroleum oil to prevent the sparking across, which would otherwise ensue from the high potential attained. The ends of this primary coil are attached to the terminals of a plate condenser. The latter is built up of 12 plates of glass, 5 in. by 12 in., with alternate sheets of tin foil. The other two ends of the primary are attached to the terminals of a rotary spark gap. In turn, these terminals are attached to the terminals of a six-inch induction coil, the primary of which was excited by transforming down the 110 volt 60 cycle alternating current to about 12 volts.

The oscillations set up in the secondary of the Tesla circuit induce corresponding oscillations in the wires pp, which extend out from the loop R surrounding e e for about 60 cm. and are soldered into two brass tubes m m about 2 1/2 mm. diameter and 25 cm. long. n n are two copper wires 1 mm. diameter and 40 cm. long, terminating in a piece of ebonite. n n slide in and out of the brass tubes m m, thus shortening or lengthening the circuit. The circuit is completed by the condenser C which is placed across the ends of the wires n n. The ebonite piece is fastened to a block of wood which slides in a groove along beside a meter stick. In this way the exact length of the circuit BC can readily be measured. For the comfort of the operator the wires connecting the Tesla coil secondary with the wires e e are enclosed in glass tubing to prevent brushing and the formation of ozone.

The condenser, fig. 3, was made from a piece of heavy capillary tubing about 6 mm. outside diameter and 3 mm. inside diameter, by blowing a bulb of 1.2 mm. diameter on one end. Through the sides of this bulb two platinum wires were sealed. Some bulbs of this type were able to stand a pressure of 115 atmospheres, the pressure of ammonia at its critical temperature. However, explosions of considerable violence sometimes occurred at lower pressures.

The following mixtures of acetone and benzene were used as standards in calibrating the condensers. The dielectric constant of these mixtures were determined by Drude+.

Composition		K at 19 C.
Acetone %	Benzene %	
100.00	0.00	20.5
84.84	15.16	17.3
67.52	32.48	13.9
48.88	51.12	10.1
34.90	65.10	7.0

A bulb, having been calibrated, was carefully dried and the air inside replaced with ammonia gas. The bulb was then immersed in a vessel containing liquid ammonia and the bulb filled by condensing the liquid inside the bulb. This was done by applying doubly distilled ammonia gas, dried with metallic sodium, to the tube under a pressure sufficient to liquefy the gas at that temperature. The bulb was then cooled in liquid air and the top sealed off.

+ Zeit. für Phys. Chem., 23, 288.

Several serious experimental difficulties were encountered in determining the resonance position from the maximum illumination of the Geissler tube. One troublesome factor was the continual flicker of the light in the tube. The introduction of a rotary spark gap into the primary of the Tesla circuit instead of an ordinary straight gap gave a much better effect. This spark gap was of the type in common use in Wireless Telegraphy to produce an even tone. An aluminium wheel, 6 in. in diameter and with 12 flat edged teeth on its circumference, is mounted upon the insulated shaft of a small inductive motor. Two rods, also aluminum, approach the circumference of the wheel in a horizontal position. As each tooth passes one of these rods, a discharge takes place and, due to the rapid motion of the wheel, is rapidly quenched out. The net result is a steady series of rapid discharges, which set up correspondingly steady oscillations in the secondary circuit.

In order to secure illumination in the vacuum tube it was necessary that the two circuits, e e and 1 1, be closely coupled. This was unfortunate for two reasons. In the first place, close coupling leads to the production of two oscillations in the secondary circuit, differing somewhat in phase and frequency.+ Two positions for maximum illumination are thus produced causing confusion.

\+ V. Bjerknes, Wied. Ann. 1895. vol. 55, p. 121.

In the second place, the tuning of the two circuits was much more difficult when they were closely coupled. This was important because of a continued shifting of the zero point or position of resonance with the condenser replaced by a wire. Thus if a condenser was calibrated for one wave length, it was always necessary to tune the circuit to that wave or otherwise the calibration would not hold.

A method of tuning after Drude+ was attempted. A variable condenser was made, fig. 3, the plates of which were brass disks 10 cm. in diameter. These were fastened to the two horizontal arms h h by the vertical pieces t t insulated by the ebony rods t' t'. The arms t t move horizontally upon h h, so that the distance between the two plates could be easily varied. The plates were attached to the points e e, fig. 1, by the wires b b, and the whole condenser immersed in oil. The circuits could then be slightly tuned by varying the capacity of the condenser. It was found that a better arrangement was the coupling of the two circuits electrostatically by placing the condenser across the points p e. The introduction of this electrostatic coupling also greatly added to the steadiness of the illumination in the vacuum tube.

With all factors favorable, the position for resonance could be determined to within one millimeter. In order

+ P.Drude, Ann. der Phys. u Chem., 1902, p. 293.

that the percentage of error might be as small as possible, as long a wave was desired as was convenient to handle. The length of the half wave was 70 cm. The corresponding frequency would be 2.1 times 10^8. From the curves I and II, it is evident that an error of 1 mm. in setting would give an error of 0.15 to 0.2 in the value of K.

An effort was made to obtain constant temperatures by heating the condenser tube over a bath of liquid kept at its boiling point. If this was done the vapor would invariably condense on the platinum lead wires of the condenser, run along them and thus spoil their contact with any connecting device which could be arranged.

Also the capacity of the condenser was considered to be in the form

$$C = C^{\circ} + KC'$$

due to the fact that some of the Faraday tubes connect through the air. Now if the air be replaced by some other vapor with the dielectric constant K_2 the capacity would be in the form

$$C = K_2 C^{\circ} + KC'$$

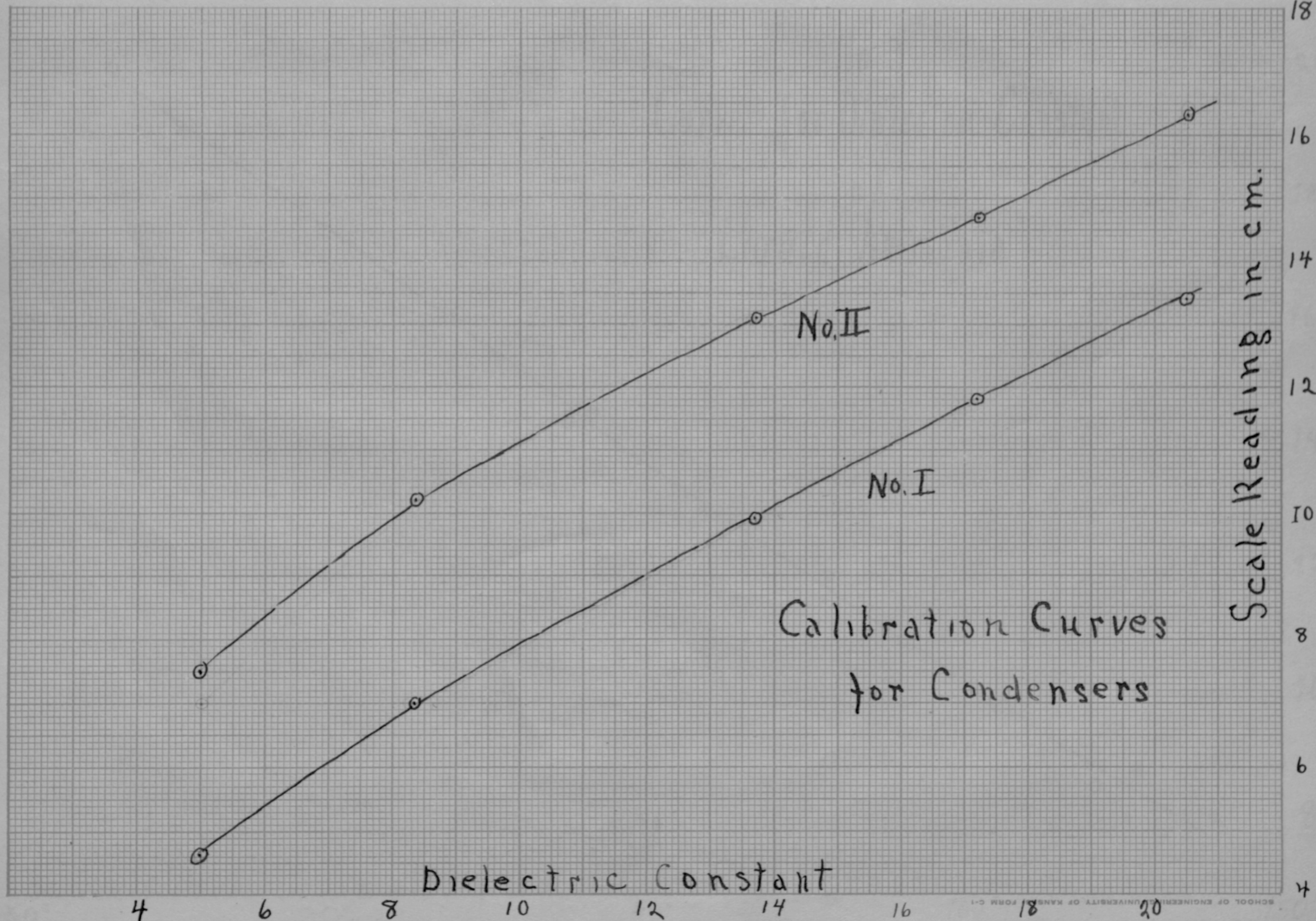
and thus dependent upon the dielectric constant of the vapor. For these reasons an air bath was used to heat the ammonia. Due to the slight change of the dielectric constant of air with change of temperature, the error mentioned above would also apply here but is doubtless small in this case.

The heating device was a simple arrangement consisting of a glass tube wrapped with a thin sheet of asbestos and wound with a dozen turns of nickle-crome wire, No. 16. A small coil of the same wire was placed in the bottom of the tube. An error of one degree in temperature produces an error of about 0.1 in the dielectric constant of liquid ammonia.

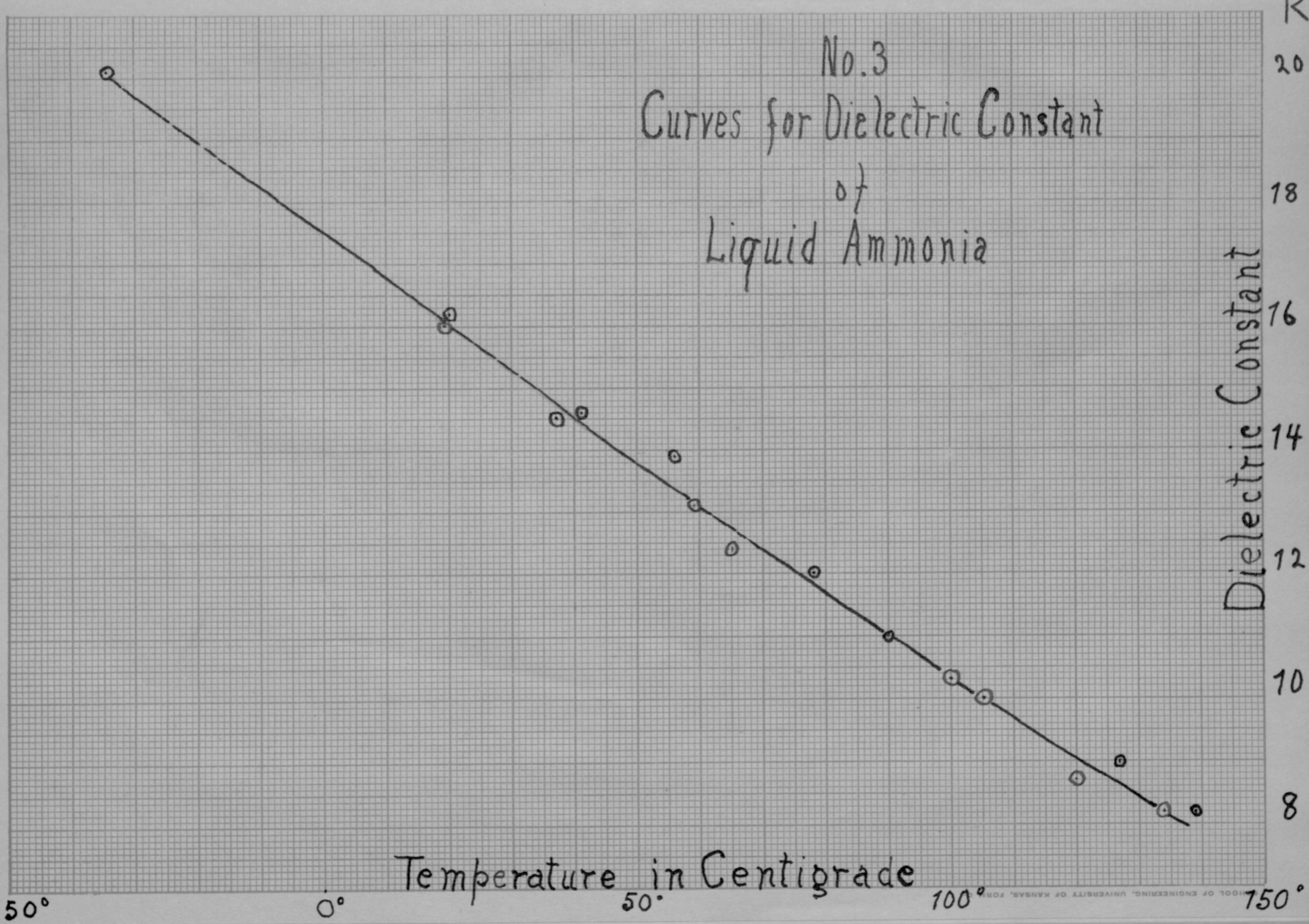
To measure the dielectric constant at the boiling point of liquid ammonia a small Dewar flask was used, with platinum wires sealed through the walls. This was calibrated and used in the same manner as the bulbs.

Below is given typical sets of data for two different condensers:

	Temp.	Scale Reading	K
First Condenser	20 C.	11.3	16.2
	37	10.3	14.5
	41	10.4	14.6
	78	9.0	12.6
	90	8.4	11.0
	127	7.4	9.0
	139	6.9	8.2
Second Condenser	19 C.	14.2	16.0
	59	12.9	13.1
	65	12.5	12.4
	100	11.4	10.3
	105	11.2	10.0
	120	10.4	8.7
	134	10.2	8.2



Calibration Curves
for Condensers
No. II
No. I
Scale Reading in cm.
Dielectric Constant
4
6
8
10
12
14
16
18
20
4
6
8
10
12
14
16
18


No. 3
Curves for Dielectric Constant
of
Liquid Ammonia
K
20
18
16
14
12
10
8
Dielectric Constant
Temperature in Centigrade
50°
0°
50°
100°
150°

Curve III has been plotted from the above data. Other determinations give further points falling upon the curve.

The following is a comparison of points on the curve with all other known values of the dielectric constant of liquid ammonia at corresponding temperatures:

Temp.	K	K (Other Observers)	
-34.5 C°.	21.0	22.0	Goodwin and Thompson+
		20.5	Rodebush ++
+14	16.4	16.2	Coolidge +++
19	16.0	16.0	Rodebush
35	14.8	15.1	"
56	13.4	14.1	"
80	11.7	11.6	"
100	10.3	——	
131	8.5	——	

\+ Phys. Rev. 838, 1890.
++ Thesis, Univ. of Kansas, 1914.
+++ Ann. der Phys. u Chem., 69, 125, 1899.