The Dielectric Constant of Liquid Ammonia

by W. H. Rodebush

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A thesis submitted to the Chemistry Department and the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of Master of Arts.

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June I9I4

The object of this research was to determine the dielectric constant of liquid ammonia over a considerable range of temperatures; if possible, from its boiling point, - 33.5°C., to its critical temperature, 131°C. The dielectric constant has been determined at -34°C by Goodwin and Thompson[1] and at 14°C by Coolidge[2]. As far as is known, these are the only determinations that have been made and it was with the object of checking these results and carrying the determination to much higher temperatures that this work was undertaken.

This work is part of the work which is being carried on, under Doctor Cady's direction, upon liquid ammonia. The ultimate object of this research is to determine if there be any relation between the degree of dissociation of a salt in an electrolyte and the dielectric constant of the electrolyte itself. By an electrolyte, we understand a substance that becomes a conductor of electricity when salts are dissolved in it. The reason for the choice of ammonia as an electrolyte to be investigated is not so evident at first glance, as ammonia can only be kept in the liquid state at ordinary temperatures under considerable pressure.

[1] Phys.Review, 8, 38, 1899
[2] Ann.der Physik und der Chemie, 69, 125, 1899

Ammonia, however, has far less solvent action 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; whereas, water, under similar circumstances, would attack the substance of which the vessel was made and dissolve a considerable amount, thereby becoming contaminated.

The relation which might be expected to exist between the dielectric constant of an electrolyte and the dissociation power of the same medium will become apparent if we consider what is meant by dielectric constant. Suppose we have two equal and opposite charges of electricity, e and e', separated by a distance d in aid. Then an attracting force will exist between the two, which will be represented, provided the proper units are used, by the formula,

$$f = \frac{e\, e'}{d^2}$$

Now, if we replace air as the medium between the two charges by another substance, such as paraffin oil, we should find the attractive force between the two charges to be only one-half of what it was in air; if we substitute acetone, the force would be but one-twentieth, and, if we substitute water, only about one-eightieth. The expression for the force exerted between two charges then becomes,

$$f = \frac{e\ e'}{Kd^2}$$

where K depends upon the medium which separates them and varies from I , in the case of an ordinary gas, to 95, in the case of hydrocyanic acid.

Now, according to the ionic theory, when a salt, such as sodium chloride, is dissolved in water, it dissociates into the two ions, Na with a positive charge of electricity, andCI with a negative charge. Nernst[I] was one of the first to point out that whatever dissociation takes place must be due to the resultant action of two forces,- first, a repelling force between the two ions of whose nature we know nothing, but which the kinetic theory of gases would explain as being due to rapid vibration; second, the attractive force between the unlike charges of electricity on the two ions. This, we see, varies inversely as the dielectric constant of the medium, in which the salt is dissolved. Hence, the greater the dielectric constant of an electrolyte, the greater dissociation would be expected. This seems to be confirmed by the fact that all liquids in which dissociation takes place

[I] Zeitschrift für Phys.Chem.,I3, 53I, I894.

to a considerable extent have high dielectric constants, of which the following are examples:

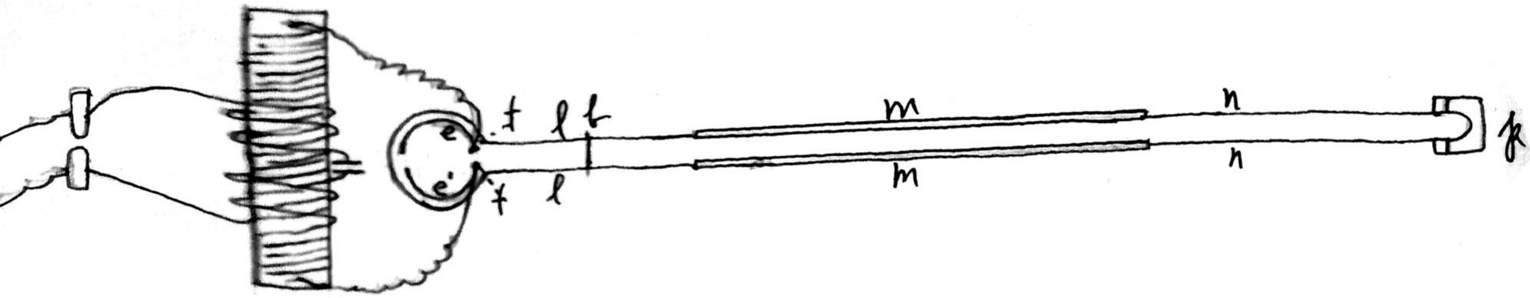
Sulfur dioxide,	dielectric	constant,	I3.75
Formic acid,	"	"	57
Ammonia	"	"	I6
Hydrocyanic acid	"	"	95
Water, which is the most familiar of dissociating solvents			80

It is not possible, however, to trace any definite relationship between dissociating power of different solvents and their dielectric constants. This is probably because of other factors which vary from solvent to solvent. If, however, we measure the dielectric constant of a solvent over a range of temperatures great enough so that its value changes considerably, and obtain the degree of dissociation of some salt over the same temperature range, then we should be able to observe any relationship that existed between the two. It was with this purpose in view that the work was begun upon liquid ammonia.

The method d,used in making the measurements, was the one devised by Drude[I], using electric oscillations of high frequency. Some modifications, which

[I] Zeit.für Phys.Chem.,23, 267, I897, 40,635,I90I.

[I] Ann.der Phys. u Chem. 6I, 467, I897.


f
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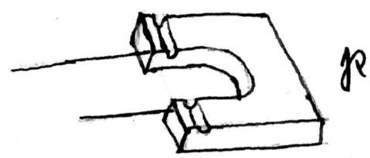
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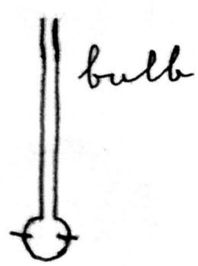
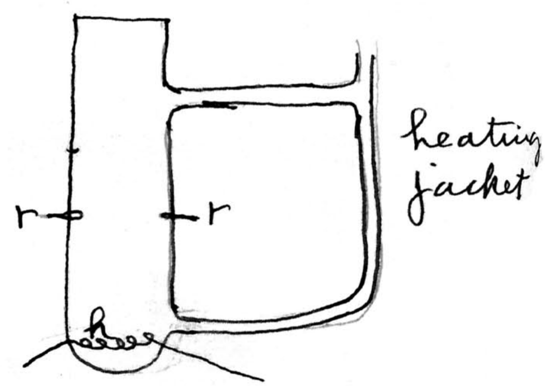

bulb


heating jacket
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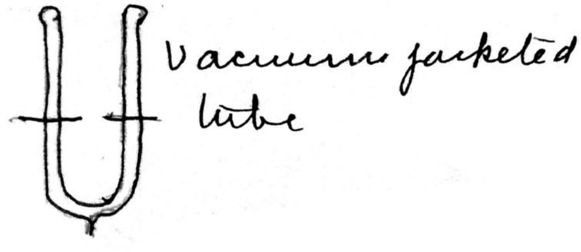

Vacuum jacketed tube

seemed to be advantageous,were made in the apparatus.

In this method, the liquid, whose constant is to be measured, is used as the dielectric of a small condenser, which is a part of the circuit in which very rapid electric oscillations are excited. For rapid oscillations, liquids, like ammonia, which ordinarily have considerable conductivity, become practically non-conducting and admit of the measurement of the dielectric constant,- a thing which would be impossible with currents of low frequency, because of their conductivity.

An outline of the apparatus appears on the opposite page. Essentially, it consists of two independent metallic circuits. In the first circuit, electric oscillations are set up by the inductive method devised by Blondlot[I]. e e′ are two semicircles of copper wire, 2 mm. in diameter, which form a circle about 5 cms. diameter. The read ends of these semicircles are separated by a gap of four millimeters; the front ends terminate in brass balls which form a spark gap of about I mm. length. ee′, 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.

I Journal de Physique ser, 2 Vol. X, p. 549.

The spark balls, f f, are connected to the terminals of the secondary of a Tesla coil. The secondary of this coil consists of about I50 turns of I 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 one centimeter. The whole coil is immersed in oil to prevent the sparking across, which would ensue otherwise from the high potential attained. Two ends of this primary coil were attached to the terminals of a Leyden jar and the other two ends to the terminals of a zinc spark gap. In turn, these terminals were connected to the terminals of a six inch spark coil, the primary of which was excited by transforming down the II0 volt 60 cycle alternating current to about I2 volts. The second metallic circuit is simply an extension of the first beyond the bridge b. The wires, l l , extend out from the loop surrounding e e' for about I0 cms. and are soldered into two brass tubes about 2½ mm. outside diameter, and I½ mm. inside diameter, 25 cms long. N n are two copper wires, I mm. diameter and 25 cms. long, terminating in a piece of ebonite,p, which 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 condenser is simply a thick glass bulb about I.4 cms. outside diameter, with platinum wires sealed through the sides, forming the condenser plates, which is filled with the liquid whose dielectric constant is to be measured. In order that different temperatures may be maintained, it was necessary to construct a heating jacket for the condenser bulb, which is shown in the drawing. It is of glass. r r are two loops of platinum wire sealed through the glass, in which the terminals of the condenser hook when the bulb is placed in position. The ends of the wires r r rest in the grooves in the ebonite plate on the wires n n . h is a heating coil, which is sealed into the bottom of the jacket. The different temperatures,at which the measurements were made, were obtained by using a series of liquids of different boiling points. Enough of a liquid was placed in the bottom of the heating jacket to cover the heating coil, and the current passed through the coil. The liquid boils and the vapor soon brings the bulb to the boiling temperature of the liquid.

The ebonite piece p 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 p b can be readily measured. The wires n n are amalgamated through-out their whole length to insure good contact.

The apparatus works as follows: The induction coil sets up oscillations in the circuit composed of the zinc spark gap, the primary of the Tesla coil and the Leyden jar. These oscillations induced currents of high potential in the secondary of the Tesla coil, which charge the spark balls f f,alternately,to high potential. When a certain potential between the spark balls is reached, the oil gap breaks down and a current oscillates back and forth in e e across the spark gap f f,inducing electric waves in the surrounding loop of wire. These oscillations are rapidly damped out but are renewed by the opposite spark ball, being charged to a high potential by the Tesla coil and the whole process is repeated a great many times in a second, so that practically a continuous oscillation takes place between the spark balls. At any instant, we may consider that a wave of positive electricity starts down one side of the loop of wire in the oil and a negative wave on the other side. These two waves intersect at b, producing a node of potential and a loop of current. Now, the circuit b - p has sympathetic waves set up in it,due to the bridge b being a common part of the two circuits. The nearer the circuit is in resonance with the exciting circuit, the more intense will be these waves. By the circuits being in "resonance" we mean having the same period of oscillation. That is, the length of the circuit b - p must be such that a wave will travel down one side of the circuit, be reflected at p, and get back to the bridge in time to reinforce the next wave of like sign that starts down the other side of the circuit. If a straight wire is laid across the wires n n at p,a wave will be reflected with full value but with opposite sign. For perfect resonance, the distance p - b is then one-half wave length which, in this apparatus, is in the neighborhood of 35 cms. This position of p is called the zero point. The position of resonance is determined by laying a Geissler tube across the wires half way between p and b. The mid-point of the wires is a loop of potential and,with the passage of each wave,a maximum difference of potential is reached, which gives rise to a glow. At perfect resonance, the tube gives a maximum lighting. In order to determine this, it is necessary to work in the dark.

If the straight wire at p be replaced by a condenser bulb, the position of p for maximum lighting will be, in general, some distance farther from b than the zero point ; the smaller the capacity of the condenser, the farther from the zero point. This will be evident from the following considerations:

The differential equations that hold in a circuit containing inductance L and capacity C, and in which the resistance is negligible,are:-

$$O = L \frac{di}{dt} + V \quad (I)$$

$$I = C \frac{dV}{dt} \quad (2)$$

Solving these equations with the conditions that, when,

$$t = O$$

$$V = Vo$$

we get,-

$$V = Vo \quad \cos \left(\frac{t}{\sqrt{Lc}} \right)$$

which is the equation for an oscillation of potential with a period of 2 $\sqrt{Lc}$.

For resonance, our circuit must behave precisely as it would if there were still a wire bridge across the wires at the zero point and we had two adjacent circuits,- the one from b to the zero point, and the second from the zero point to the condenser. Now, for resonance the value of the radical $\sqrt{Lc}$ for the last circuit must be equal to the value for the first circuit. As c decreases, then L must be increased, which is done by lengthening the circuit. If we represent the distance of p from the zero point for resonance with the bulb in position,by l and the wave length by λ , then ,

$$\cot 2\pi \frac{l}{\lambda} = N_0 + KN$$

Where No and N are constants depending upon the bulb used, and K is the dielectric constant of the liquid.

This formula is derived in the following manner[I]:-

A periodic wave of electricity set up in a wire may be represented by the equation,

$$(I) \quad E = e^{-\gamma\left(\frac{t}{T} - \frac{z}{\lambda}\right)} \cos 2\pi\left(\frac{t}{T} - \frac{z}{\lambda}\right)$$

where E is the quantity of electricity at any time t, and at any point along the wire at a distance z from the origin. T is the time of oscillation and the wave length. Then $\lambda = CT$, where C is the velocity. Writing (I) in complex numbers,

$$)2) \quad E = e^{\alpha\left(\frac{t}{T} - \frac{z}{\lambda}\right)}, \quad \alpha = -\gamma + 2\pi\sqrt{-1}$$

Suppose, now, a condenser be placed at a position z $=\beta\lambda$, then the reflected wave will be represented by,

$$(3) \quad E' = r\, e^{\alpha\left(\frac{t}{T} + \frac{z}{\lambda}\right)}$$ wher r is the factor of reflection.

[I] An. der Physik u Chemie, 6I , 479, I897.

Now, at any point along the wire, the following equation will hold:

(4) $\frac{\partial i}{\partial z} = \frac{1}{c}\frac{\partial E}{\partial t}$ i = current

From (2) (3) and (4), it follows that the initial current

(5) $i = e^{\alpha\left(\frac{t}{T} - \frac{z}{\lambda}\right)}$

and the reflected current

(6) $i' = e^{\alpha\left(\frac{t}{T} + \frac{z}{\lambda}\right)}$

The second differential equation, which holds for two parallel wires terminating in a condenser in which waves are set up, is,

(7) $I = C\frac{\partial(V_1 - V_2)}{\partial t} + \frac{V_1 - V_2}{w}$ $V_1 = -V_2$

Where C is the capacity of the condenser, V and Va the potential of opposite plates and W the ohmic resistance.

If E is the charge per unit length of the wire, then,

(8) $V = 2\ c\ \ln\frac{d}{R}\ E$

Where d is the distance between wires and R the radius of the wires.

Differentiating (7) with respect to   and substituting from (4) and (8)

(9) $\frac{\partial I}{\partial t} = -4c^2 \ln\frac{d}{R}\left(C\frac{\partial^2 i}{\partial z\,\partial t} + \frac{1}{w}\frac{\partial i}{\partial z}\right.$

since $I = i + i^{I}$ and $z = \beta\lambda$

Then,

(10) $r = e^{-2\alpha\beta\frac{1-p}{1+p}}$

Where,

(11) $k = 4\ln\frac{d}{R}\left(c_2 C\frac{\alpha}{\lambda} + \frac{c}{w}\right)$

If we set,

$$(I2) \quad \frac{p-1}{p+1} = q\, e^{4\pi\varphi\sqrt{-1}}$$

Then,

$$(I3) \quad r = -q\, e^{2\gamma\beta}\, e^{4\pi(\varphi-\beta)\sqrt{-1}}$$

The reflected wave will reinforce the initial wave when

$$(I4) \quad \beta = \varphi + \frac{h}{2}$$

Where h is a whole number or zero.

The value of β determines the distance of p $\beta\lambda$ which causes maximum lighting of the vacuum tube. In this apparatus, h = I.

Then,

$$(I5) \quad \frac{l}{\lambda} = \beta - \frac{1}{2} = \varphi$$

(I6) If we set $p = a + b\sqrt{-1}$

Then,

$$(I7) \quad \begin{cases} a = 4 \ln \frac{d}{\rho}\left(\frac{c}{\omega} - \gamma\frac{C'}{\omega}\right) & C' = c^2 C \\ b = 4 \ln \frac{d}{\rho}\, 2\pi \frac{C'}{\lambda} \end{cases}$$

From (I2),

$$(I8) \quad q^2 = \frac{a^2+b^2+1-2a}{a^2+b^2+1+2a} \qquad 0 < \varphi < \frac{1}{4}$$

$$(I9) \quad \tan 4\pi\varphi = \frac{2b}{a^2+b^2-1} \qquad 0 < \varphi < \frac{\lambda}{4}$$

$$(20) \quad \tan 4\pi\frac{l}{\lambda} = \frac{2b}{a^2+b^2-1} \qquad 0 < l < \frac{\lambda}{4}$$

If we assume W the ohmic resistance infinitely large, then neglecting a^2 and γ^2,

$$(21) \quad \cot 2\pi \frac{l}{\lambda} = b = 8\pi \ln \frac{d}{R} C'$$

C^I, the capacity of a bulb filled with liquid, may be represented by the expression,

$$C^I = Go + Kg$$

Where Go is the capacity of the glass and Kg the capacity due to the liquid contained in the bulb, K being the dielectric constant of the liquid.

Then,

$$\cot 2\pi \frac{l}{\lambda} = n_o + Kn$$

No and n are constants depending on the bulb used. The position of the bulb for maximum lighting is thus seen to depend upon the dielectric constant of the liquid used.

In actual practice, however, it is easier to calibrate the bulb used by determining the position of resonance for several different liquids of known dielectric constants and plotting a curve of the reading of the position of p on the meter stick against dielectric constant.

The following mixtures of acetone and benzene were used as standards, the dielectric constants of which were determined by Drude[I].

[I] Zeitschrift für Phys. Chem. 23, 288

COMPOSITION			
ACETONE %	BENZENE %	K at I9° C	K
I00	0	20.5	-.6%
84.84	I5.I6	I7.3	-.5%
67.52	32.48	I3.9	-.5%
48.88	5I.I2	I0.I	-.5%

Furthermore, since the wave length , and, hence the position of the "zero point",varied from time to ti me it was necessary, in practice, to make two separate calibrations for different positions of the zero point and from this determine the correction to be applied in case of variation of the zero point. The zero point was varied from one position to another,arbitrarily,by bending the loop of wire surrounding the spark gap into a larger or smaller circle.

A bulb, having been calibrated, was cooled by immersing it in a vessel containing liquid ammonia, filled with liquid ammonia until the surface of the liquid rose into the stem and the top was sealed off. The bulb was then ready for readings to be taken.

In the actual operation of the apparatus, various difficulties were encountered and which were overcome, more or less, successfully. One of the first difficulties was the flickering and unsteady lighting of the Geissler tube, which made it impossible to determine the settings for maximum lighting with any degree of accuracy. This was found to be due to the formation of bubbles of gas in the oil in the spark gap, which seemed to interfere in the passage of the spark. This was overcome by arranging a turbine pump, operated by a motor, which forced a jet of oil between the spark balls and kept up a steady circulation of the oil. With this arrangement, the lighting of the tube became quite steady.

So much ozone was generated by the brushing caused by the high potential, that it was found necessary for the comfort of the operator to enclose the leads from the Tesla coil to the spark gap in glass tubes and to build a hood over this part of the apparatus.

The greatest difficulty met with in working the apparatus was to get a sharp maximum in the lighting of the Geissler tube. With the apparatus working at its best, the range of positions of the bulb, for which the tube gave a maximum lighting without perceptible variation, extended over a distance of about three millimeters. It was necessary to measure these two extremes of position and assume the point halfway between as the exact setting for resonance. In order to obtain any degree of accuracy, repeated readings, at least five in number, were taken. The fact that the greatest variation in the setting for resonance,as obtained from the different readings, was always less than one millimeter would indicate that the error in setting was less than one millimeter. An error of one millimeter in the setting would cause an error of about 0.3 in the value of the dielectric constant as read from the curve. At ordinary temperatures the value of K for liquid ammonia is about I6; hence, the error would be something less than 2 %.

Measurements were taken at the boiling point of liquid ammonia -34.5° C., room temperature, I9°; the boiling point of ether, 35°; the boiling point of acetone, 56°, and the boiling point of benzene, 80°. To measure the dielectric constant at the boiling point of liquid ammonia, a small double walled, vacuum jacketed flask was made with platinum wires sealed through the walls. This was calibrated and used in precisely the same manner as the bulbs, except that, when filled with ammonia, the tube was closed only by a cork through which passed a tube of small bore.

In heating the sealed bulb, a difficulty was encountered in that vapor would form in the bulb, and force the liquid up into the capillary stem, leaving the bulb only partially filled with liquid. This was overcome by surrounding the upper end of the capillary stem with a coil of wire and heating to a high temperature when the vapor formed above forced the liquid back down into the bulb.

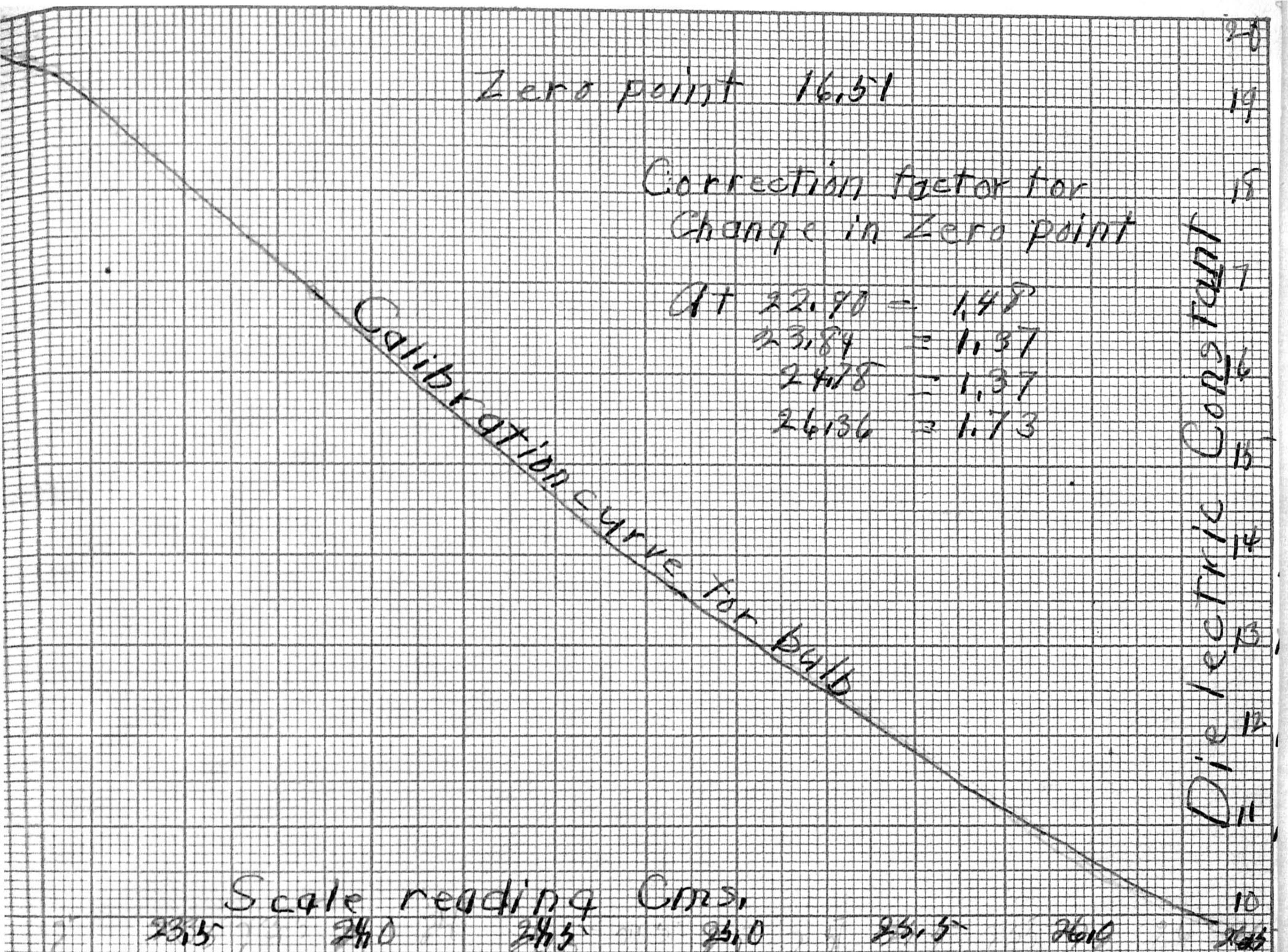
Special precautions were taken to obtain pure dry lqiuid ammonia by distilling it over sodium.

The following results were obtained as the average of repeated readings:-

Temperature	K	K(Other observers)
-34.5^{o}	20.5 ± .3	22.(Goodwin & Thompson (Phys.Rev.838,I899)
+I9.	I6.0 ± .3	I6.2(At I4^{o}.Coolidge (Ann.der Phys.in (Chem. 69,I25,I899
35	I5.I ± .3	
56	I4.I ± .3	
80	II.6 ± .3	

The measurements have not been carried above 80^{o} for the reason that so far no bulb has been made strong enough to stand the pressure exerted by the liquid ammonia at temperatures above 80^{o}. At 80^{o} the pressure is in the neighborhood of 60 atmospheres.

The results obtained leave something to be desired in the way of accuracy, owing to the large probable error. It is my intention to check over the determinations that have already been made and to carry these measurements on up to the critical temperature, I3I$^{\circ}$ at which ammonia has the very considerable vapor pressure of II5 atmospheres.


Zero point 16.51
Correction factor for
Change in Zero point
At 22.90 = 1.48
23.84 = 1.37
24.78 = 1.37
26.36 = 1.73
Calibration curve for bulb
Scale reading Cms.
23.5
24.0
24.5
25.0
25.5
26.0
26.5
Dielectric Constant
10
11
12
13
14
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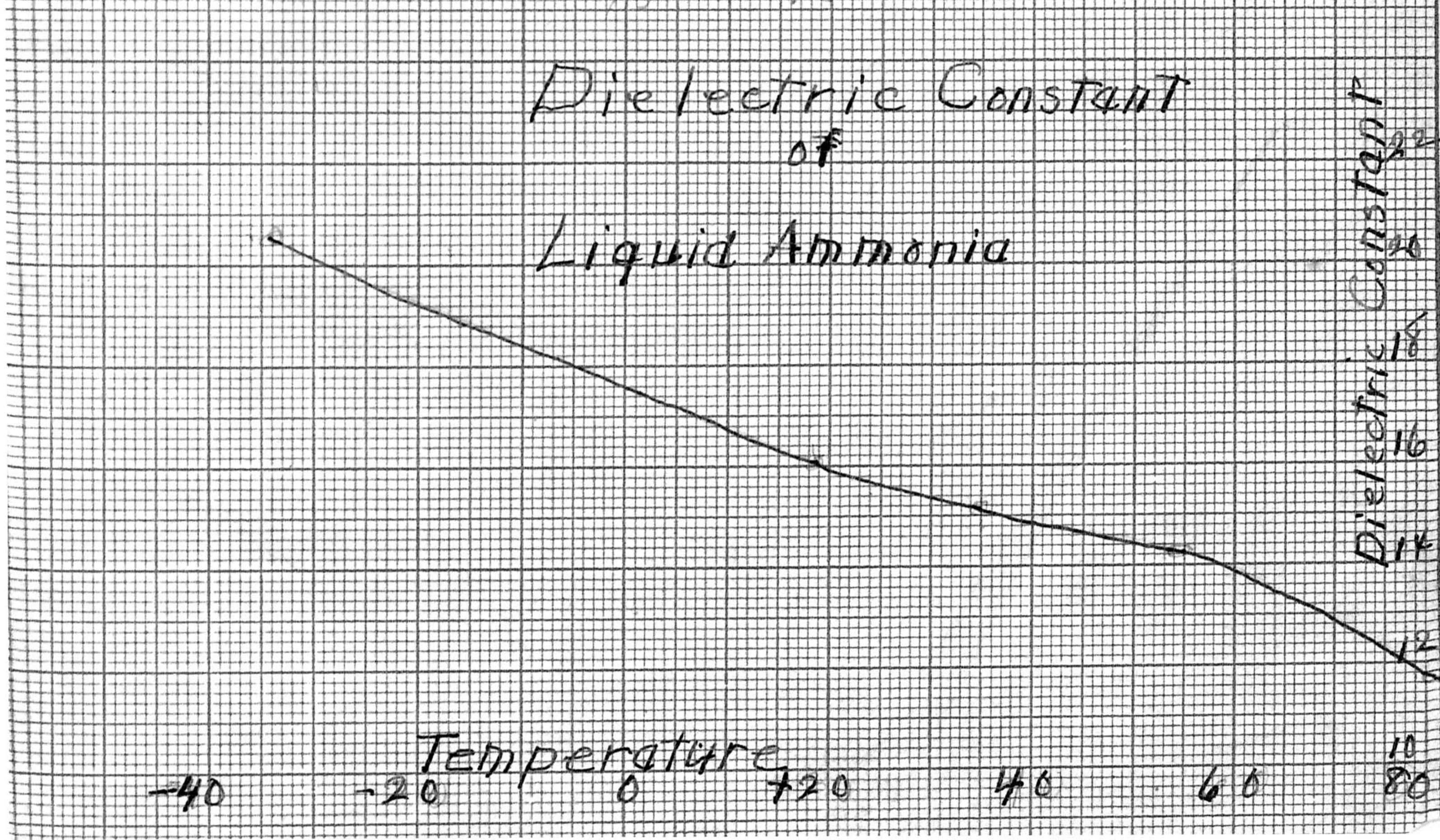
Dielectric Constant
of
Liquid Ammonia
Temperature
-40
-20
0
+20
40
60
80
Dielectric Constant
10
12
14
16
18
20
22