or $Na[Al(NH_2)_4]$. This compound loses one molecule of ammonia on heating in a vacuum above 90°. The equations for the reaction have been shown to be $Al + 3NaNH_2 \rightleftharpoons Al(NH_2)_3 + 3Na$; $Al(NH_2)_3 + NaNH_2 = Al(NH_2)_2NHNa.NH_3$; $3Na + 3NH_3 = \frac{3}{2}H_2 + 3NaNH_2$.

The action of potassium amide on amalgamated aluminum and on magnesium are analogous in character. An explanation is given which depends upon the fact previously pointed out by Kraus that dilute solutions of the alkali metals in ammonia are salt-like in character. The initial stages may be regarded as metatheses, although actually involving equilibria which suffer continual displacement because of secondary reactions.

2. A solution of sodium in liquid ammonia reacts with amalgamated aluminum to form the same sodium ammono-aluminate described above. Sodium amide is probably first formed, and this in turn reacts according to the equations given. The mercury of the amalgam does not play an essential part in the reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

THE DIELECTRIC CONSTANTS OF ORGANIC LIQUIDS AT THE BOILING POINT

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The following study was undertaken with the idea of finding some relationship between the dielectric constant of liquids and other physical properties. It was thought that the dielectric constant would be found to be related to those properties of liquids that depend upon the force of molecular attraction, namely, latent heat of vaporization, surface tension, etc. That such relationships do exist is shown by the parallelism that is exhibited in the case of organic homologs.[1,2,3] The conclusion was, however, reached that no simple relationship exists between the dielectric constant and the latent heat of vaporization although in the case of closely related liquids there was unmistakable evidence to show that the contrary is true. Walden[4] connects several physical properties of liquids with the following function of the dielectric constant: $\frac{\text{D.C.} - 1}{\text{D.C.} + 2}, \frac{1}{\delta}$ which according to the Clausius-Mossotti theory involves the volume actually occupied by the molecules. All of these relations give different values for associated and non-associated liquids. Walden uses values of surface tension, latent heat of vaporization, etc., at the boiling temperature, while the values of

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[1] Hesehus, *Physik. Z.*, [2] 750 (1900).

[2] Campbell, "Modern Electrical Theory," Cambridge University Press, **1913.**

[3] Obach, *Phil. Mag.*, [5] **32,** 113 (1891).

[4] Walden, *Z. physik. Chem.*, **70,** 569 (1910).

the dielectric constant and density are taken at 20°. This procedure was justified on the ground that according to the Clausius-Mossotti theory the above function is independent of the temperature. However, Katz[5] has shown that the function in question is not independent of the temperature but gives variations that are especially marked with liquids of high dielectric constant.

If we accept the classical electronic theory of dielectrics, we arrive at the following picture: the dielectric constant is due to a displacement of a certain number of electrons by the electric field. The following relation is given by Lorentz and Lorenz as expressing the connection between the dielectric constant and the number of displaced electrons N, the charge on an electron e and the force f due to the positive charge of the molecule which tends to restrain the electron from leaving.

$$\text{D.C.} = 1 + \frac{4\pi\ Ne^2}{f - {}^4/_{3}\pi\ Ne^2}$$

Thus we have two unknown quantities, N and f; N is probably proportional to the number of molecules and therefore to the density of the substance, but little or nothing is known of the force f. It is probable that this force is connected with the force of molecular attraction, and hence the relation that is sought between the dielectric constant and surface tension or latent heat of vaporization.

It has been suggested that more constant relations might be obtained if values of the dielectric constant were taken at the boiling temperature. This has been attempted by Turner[6] with a few liquids by calculating the dielectric constant at the boiling point from the values at 20° and the temperature coefficient. However, the dielectric constant is not a linear function of the temperature, as has been shown by Katz and others, and in certain cases behaves in a most irregular manner. For example, Tangl[7] has shown that the dielectric constant-temperature curve for ether is first convex and then concave toward the temperature axis. For this reason we have therefore undertaken to determine directly the dielectric constant at the boiling temperature. Thirty-five organic liquids in all were measured, and the results should be of the greatest value to anyone interested in the theory of dielectrics.

Measurements of the dielectric constant at the boiling point are not easily made due to the troublesome effect of conductivity, which increases very rapidly with increasing temperature. The method used in the following measurements has enabled us to work with liquids having a conductivity less than that of pure water, without sacrificing the accuracy of the results.

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[5] Katz, *Z. physik. Chem.*, **19**, 94 (1896).

[6] Turner, *J. Chem. Soc.*, **107**, 276 (1915).

[7] Tangl, *Drude's Ann.*, **10**, 748 (1903).

Apparatus.—The method employed was a modification of the Nernst bridge method which has been described in detail by King and Patrick.[8] With the exception of a different arrangement of the dielectric cell, very few changes in the apparatus were necessary. The dielectric cell consisted of two coaxial platinum cylinders sealed in a fixed position by small plugs of glass at both ends. This condenser was suspended in the liquid by means of two platinum wires. The size of the cylinders of cell No. 1 were 6.3×1.9 cm., and 6.3×2.2 cm. With this cell we were able to read changes of about forty in the dielectric constant. In using cell No. 2, in which the plates were closer together (the outer cylinder was 2.1 cm. in diameter) the same change on our reference scale corresponded to a change of about ten in the dielectric constant. This latter cell could only be used with non-associated liquids or at least with liquids of low conductivity.

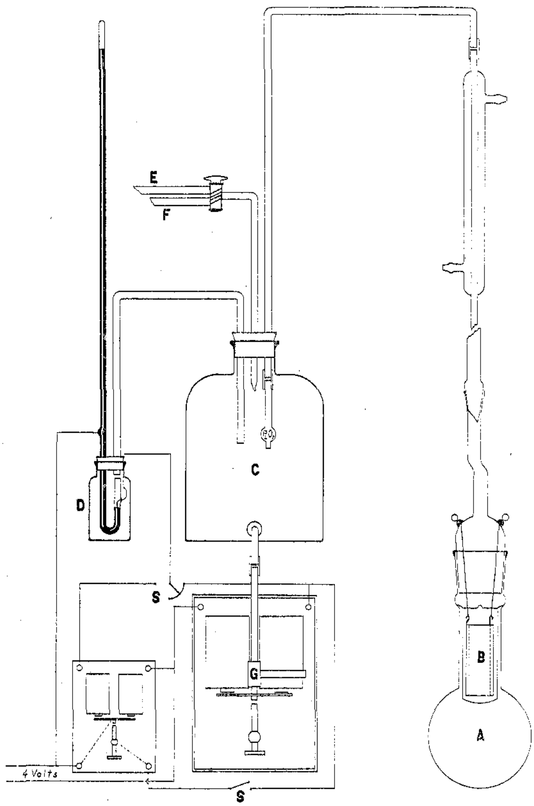

Fig. 1

The liquid dielectric was brought to its boiling temperature by being immersed in a bath of its own vapor at a pressure of 760 mm. This pressure was held constant to within less than 1 mm. by means of a pressure regulator. The boiling flask (A) in Fig. 1 had a capacity of about 250 cc. and the dielectric cup 50 cc.; consequently, the minimum amount of liquid required for a determination was approximately 150 cc. The glass cup was suspended within the neck of the flask by means of four prongs, which allowed the vapor to pass around the cup into the condenser above. The cell (B) was suspended within this cup by two platinum wires sealed in at the top of the ground-glass stopper. Care had to be taken to prevent superheating of the vapors surrounding the dielectric cup. The reading was taken when the liquid in the cup had reached such a temperature that an occasional bubble would rise from the bottom. This very slow boiling did not affect the location of the minimum, since the bubble did not pass between the two plates. This was found to be the criterion of the correct boiling temperature by a preliminary experiment in which the platinum cell was replaced by a standard thermometer and the boiling temperature of water observed.

By means of a slight bend in the tube leading from the flask to the condenser, it was possible, by giving the condenser a half turn in the ground-glass joint, to cause the refluxing liquid to drop directly into the cup or to run down the side of the flask as desired. This arrangement was to allow for refilling the cup in case an appreciable amount

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[8] King and Patrick, THIS JOURNAL, 43, 1835 (1921).

of the liquid had evaporated before the final reading was obtained. The liquid was never allowed to reflux into the cup while a bridge reading was being taken, since this resulted in a shifting of the minimum due to the cooling effect of the condensed liquid.

The top of the condenser was connected to the equalizing bottle C of the manostat by means of glass tubing. The liquid was protected from the moisture of the air by a tube containing phosphorus pentoxide connected inside the bottle C. At the top of the equalizing bottle was a glass tube which could be connected either to the compressed air line or to a water suction pump at E and F. A third tube was connected with a bottle D containing the open end of a barometer. The mercury valve G of the gas regulator was attached to the bottom of the equalizing bottle.

The mercury in the barometer was so adjusted that when contact was made with the platinum wire sealed in at the lower limb, the height was exactly 760 mm. The barometer was calibrated both by determining the pressure at which pure water boiled at 100° and also by comparison with a standard barometer. When the atmospheric pressure was less than 760 mm., the system was connected with the pressure lines, and the electric connections were made as shown in the drawing. Thus when the circuit was broken between the mercury meniscus and the platinum point, the valve G opened and allowed the air to escape. By careful regulation of the air entering and leaving, the fluctuations of the mercury meniscus were reduced to less than 0.5 mm. In the case that the atmospheric pressure was greater than 760 mm. the system was connected to the reduced-pressure sides, and the second relay thrown in by means of the switches S and S′. We were therefore able to bring the pressure to the value 760 mm. under all conditions of atmospheric pressure. The two relays were actually enclosed in a double walled box not shown in the drawing. This was to prevent the noise of the relays from interfering with the location of the minimum on the bridge.

Calibration.—The calibration of the scale was made by using different standard liquids whose dielectric constants at room temperature were accurately known. The temperatures of the standard liquids were ascertained by allowing them to come to the temperature of the room in contact with a standard thermometer. The temperature was taken immediately before and after the bridge reading was made. The values of the known dielectric constant when plotted against the scale reading of the measuring condenser gave an exact straight line as shown by King and Patrick. This curve was plotted on a large sheet of paper (100×150 cm.) accurately coördinated in millimeters from which the values of the dielectric constant at the boiling temperature were taken. The standard liquids, the values of the dielectric constant at 18°, and the temperature coefficients are given in Table I.

TABLE I

DIELECTRIC CONSTANTS OF STANDARDS

Liquid	D. C. at 18°	$\frac{1}{D} \times \frac{dD}{dT}$	Observer
Benzene	2.288	0.0007	Turner
Chloroform	4.95	.00376	Walden
Aniline	7.115	.00351	Katz and Turner
o-Nitrotoluene	27.71	.0055	Turner
Nitrobenzene	36.45	.005	Turner

The scale of the measuring condenser was calibrated at frequent intervals during the course of this work and was tested with one or more standard liquids before and after each measurement.

Purification of Liquids

Benzene.—C. P. Benzene was shaken repeatedly with sulfuric acid until the latter was no longer darkened. It was then shaken with mercury, washed with water, dried and distilled. After two fractional crystallizations, it was dried over metallic sodium and distilled. A constant-boiling fraction was preserved.

Chloroform.—After standing for several weeks over concd. sulfuric acid, the chloroform was washed repeatedly with water, dried over calcium chloride and fractionated. A 500cc. fraction which distilled within 0.03° was preserved.

Aniline.—C. P. Aniline was twice fractionally distilled, then crystallized, dried with potassium hydroxide and again distilled. A 400cc. fraction boiling within 0.15° was taken.

o-**Nitrotoluene.**—A C. P. sample was dried with calcium chloride, fractionated once by distillation and twice by crystallization, and finally redistilled. A 300cc. fraction boiling within less than 0.1° was taken.

Nitrobenzene.—C. P. Nitrobenzene was dried with phosphorus pentoxide. A fraction boiling at 212.0–212.08° (770 mm.) was used.

The standard liquids were kept in the dark in a desiccated atmosphere under a bell jar. They were several times redried and redistilled during the course of this work.

The liquids investigated were purchased in the purest possible condition and were further purified with suitable reagents, dried, and finally subjected to one or more fractional distillations, either at normal or reduced pressures. A very efficient all-glass still, consisting of six sections of a Young "evaporator," was used. The fractions taken, boiled within a small fraction of a degree of the correct temperatures, except of those of quinoline and acetonitrile. Quinoline which had been separated from any contained nitrobenzene by steam distillation and from aniline by diazotization and subsequent steam distillation, extracted with ether, distilled, and dried over potassium hydroxide, was subjected to several fractional distillations. Nevertheless, a constant-boiling fraction could not be obtained. The fraction finally used, consisted of about 200 cc., boiling between 237.3° and 238.5° (uncorr.).

Acetonitrile was washed with water, salted out with potassium hydroxide, dried and fractionally distilled several times with phosphorus pentoxide. The fraction used boiled at 80.1–81.3°. The liquid in the dielectric cell, however, probably represents a much better sample, since the first portion only was used in the cell.

The impurity which gave by far the most trouble was water. As is well known, it is very difficult if not impossible to remove the last traces of water from certain alcohols, ketones, etc., and the presence of a very small amount will increase the conductivity of these liquids to such an extent that a minimum on the bridge cannot be obtained. Even when the liquid had a very small conductivity at room temperature, it was often the case that at the boiling temperature the conductivity was so great that it required the maximum conductance of the shunt resistances to counterbalance it.

Fleming[9] points out that there are two kinds of conductance: The first follows Ohm's law and is due to a large extent to impurities. This conductance can be greatly reduced if not eliminated entirely by proper purification and drying. The other conductance which does not obey Ohm's law, but is proportional to the frequency of the alternations, is caused by a slipping of the displaced electrons. This latter conductance increases very rapidly with the temperature, and because of this fact accurate measurements of the dielectric constant of certain liquids at the boiling temperature cannot

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[9] Fleming, *Proc. Phys. Soc.*, [2] **23,** 117 (1911).

be made. The values for acetonitrile, benzyl cyanide, ethylene chlorohydrin and nitromethane reported below have been rendered less accurate because of this conductivity.

The values of the dielectric constant at room temperature are included in Table II merely for comparison. They are reported in the first place only since no particular care was taken in their determination. The reason for this was that the temperature could not be determined accurately without exposing the liquids to the moisture of the air, which would result in a much higher conductivity and in certain cases would have prevented measurement being made at the higher temperature. It may be mentioned

TABLE II

DIELECTRIC CONSTANTS OF LIQUIDS

Liquid	D. C. at boiling point		B. P. °C.	D. C. at room temp.	°C.
Benzene	2.17	0.01	80.15	Standard (Table I)	
Toluene	2.17	.01	110.70	2.3	24
m-Xylene	2.15	.01	139.3	2.4	24
p-Cymene	2.27	.02	176.5	2.5	25
Chloroform	4.23	.01	61.20	Standard	..
Carbon tetrachloride	2.10	.01	76.74	2.2	23
Carbon disulfide	2.58	.01	46.25	2.6	25
Ethyl bromide	8.81	.02	38.40	9.4	24
Ethylene bromide	4.09	.02	131.3	4.8	23
iso-Amyl bromide	4.70	.02	120.6	6.1	25
n-Butyl iodide	4.52	.02	129.9	6.15	25
Methyl iodide	6.48	.02	42.35	7.0	24
Ethyl ether	4.11	.01	34.54	4.3	24
Ethyl acetate	5.30	.02	77.15	6.4	25
Chlorobenzene	4.20	.02	132.00	5.6	25
Aniline	4.54	.02	184.55	Standard	..
o-Toluidine	4.00	.02	199.7	6.4	26
Acetonitrile	26.2	.10	81.60	36.2	25
Benzyl cyanide	8.5	.10	233.5	18.7	27
Butyraldehyde	10.78	.02	77.0	13.4	26
Paraldehyde	6.29	.02	128.0	13.9	25
Anisaldehyde	10.38	.02	248.0	22.3	22
Acetone	17.68	.02	56.15	21.0	21
Methylethyl ketone	14.46	.02	79.60	18.45	23
Acetophenone	8.64	.02	202.0	17.75	24
Ethylene chlorohydrin	13.2	.1	132.0	25.8	24.5
Ethyl alcohol	17.30	.02	78.32	25.8	20
n-Propyl alcohol	11.83	.02	97.19	20.8	23
n-Butyl alcohol	8.19	.02	117.71	17.8	25
iso-Amyl alcohol	5.82	.02	131.6	15.3	23
o-Nitrotoluene	11.82	.02	222.3	Standard	..
Nitrobenzene	15.61	.02	210.85	Standard	..
Pyridine	9.38	.02	115.50	13.3	25
Nitromethane	27.75	.10	101	39	
Quinoline	5.05	.02	238	9.00	25

here that it was necessary to distil several of the alcohols, ketones and nitriles directly into the flask *A* in order to prevent them from being contaminated with the moisture of the air.

When cell No. 1 was used, each millimeter of the scale division of the measuring condenser represented a change in the dielectric constant of nearly 0.02, and with cell No. 2 each scale division corresponded to a change in dielectric constant of 0.01. When the conductivity was not greater than that which could be balanced out with the shunt resistance filled with Mangani solution,[10] the readings could be checked to within less than one division.

In case the conductivity was greater than this, it was necessary to add potassium chloride to the Mangani solution in the shunt resistance tubes. As a consequence the greater part of the current was shunted around the condensers and the result was that the minimum became very much fainter. This was the case with the 4 liquids in Table II where the dielectric constant was determined to within only 0.1 of a unit. In no case are values reported which could not be checked within 5 scale divisions. The few liquids worked with which could not be determined with this precision were methyl alcohol, which had too high a conductivity and showed anomalous absorption, ethyl sulfate and monochlorohydrin.

Discussion of Results

It may be stated at the outset that no improvement in the empirical formulas of Walden and others was shown after the substitution of our results for the dielectric constant at the boiling point. The agreement was no worse than that obtained by Walden, but on the other hand it was no better. From this fact one may be inclined to agree with Walden that the particular function of the dielectric constant employed by him was independent of the temperature. However, it is our belief that no generalization connecting the dielectric constant with other properties of liquids has been formulated that is worthy of serious consideration. There is hardly another property of liquids which at a corresponding temperature exhibits such wide variations as the dielectric constant. The primary object of this paper is to provide accurate data which may serve as a basis for a physicochemical generalization regarding the dielectric constant of liquids.

In those expressions which contain the Clausius-Mossotti relation, the difference in the values when applied to associated liquids is probably due to the fact that the expression, $\frac{\text{D.C.} - 1}{\text{D.C.} + 2}$, is not a correct measure of the volume actually occupied by the molecules. Furthermore, the assumption made by Lorentz that the molecules around a given molecule act with equal

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[10] Mangani solution is prepared by dissolving 121 g. of mannite, 41 g. of boric acid and 0.06 g. of potassium chloride in one liter of water. This solution has a specific conductivity of 0.9×10^{-7} and practically no temperature coefficient.

force upon it does not seem to be entirely justifiable. According to recent theories of the structure of the molecule, certain portions have stronger external fields than others. Such a theory is used by Langmuir in his explanation of surface energy, adsorption, etc. Likewise, the dipole theory of Debye[11] leads to the same conclusion. This theory attempts to explain the electrical properties of dielectrics on the assumption that in addition to the free and elastically bound electrons, there are electrical doublets or dipoles whose strength does not depend on the electric field in which they are situated. These dipoles are assumed to be the result of dissymmetry in the molecule. The theory cannot be said to be in its final form, although a recent modification by Gans[12] seems to hold great promise.

When we arranged liquids according to their value of the expression (D.C. $-$ 1)/(D.C. $+$ 2) it was found that the order did not agree with the known solubility relations or chemical properties. On the other hand, it was found by trial that the expression $\frac{(\mathrm{D.C.}/\delta) - 1}{(\mathrm{D.C.}/\delta) + 2}$ gave results of some value. We therefore decided to use this latter expression as representing the volume actually occupied by the molecules.

The application of the above idea may be illustrated by applying it as a correction to Dieterici's equation for the internal heat of vaporization. Dieterici[13] has shown that the empirical relation, $\lambda_i = CRT \log (V_2/V_1)$, where C is a constant, V_2 and V_1 are the specific volumes of the saturated vapor and liquid, respectively, and R is the ordinary gas constant referring to 1 g., holds over a wide range of temperature for normal or non-associated substances. When we substitute the free space of the molecules in the liquid state in place of V_1, we obtain an equation similar to that of Bakker,[14] namely, $\lambda_i = CRT \log (V_2/(V_1 - b))$. We, however, set b equal to $\frac{(\mathrm{D.C.}/\delta) - 1}{(\mathrm{D.C.}/\delta) + 2}$.

In Table III are given the values of the constant C as calculated from the above equation. It is surprising to notice the constancy of C even in the case of associated liquids. We do not claim that we are able to express exactly the actual volume occupied by the molecules in the liquid state, but some progress is indicated and it is predicted that further work along this line may reveal results of the greatest interest. A knowledge of the structure of liquids would certainly be of the utmost service in the elucidation of the many problems in the field of solutions, etc. It is interesting to note that the only liquids giving widely diverging values of C are the ketones and compounds containing nitrogen.

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[11] Debye, *Physik. Z.*, **13**, 97 (1912).

[12] Gans and Isnardi, *ibid.*, **22**, 130 (1921).

[13] Dieterici, *Ann. Physik*, **25**, 269 (1908).

[14] Bakker, *Z. physik. Chem.*, **12**, 670 (1893).

TABLE III

LATENT HEATS OF VAPORIZATION AND MOLECULAR FREE SPACES

Liquid	$\lambda_i + RT/M$	δ at b. p.	b	C
Benzene	94.4	0.8111	0.358	1.5
Toluene	83.55	0.7781	.373	1.5
m-Xylene	78.25	0.7572	.376	1.5
Chloroform	58.4	1.4101	.400	1.5
Carbon tetrachloride	46.4	1.4802	.123	1.6
Ethylene bromide	43.6	1.932	.272	1.5
Ethyl bromide	58.6	1.413	.636	1.3
Butyl iodide	46.5	1.430	.418	1.6
Ethyl ether	88.4	0.6968	.620	1.5
Carbon disulfide	83.8	1.223	.270	1.4
Aniline	104.3	0.8736	.583	1.45
Pyridine	101.4	0.883	.762	1.3
Ethyl acetate	83.1	0.8302	.642	1.4
Nitrobenzene	81.7	1.0071	.828	1.2
o-Nitrotoluene	75.2	0.9603	.790	1.3
Acetone	125.3	0.751	.882	1.3
Methylethyl ketone	103.44	0.732	.864	1.3
Ethyl alcohol	216.4	0.741	.882	1.5
Butyl alcohol	134.3	0.727	.774	1.6
iso-Amyl alcohol	120.9	0.715	.681	1.7
iso-Amyl bromide	53.8	1.07	.532	1.5
Chlorobenzene	73.7	0.9816	.522	1.45
o-Toluidine	95.1	0.788	.576	1.5
Quinoline	82.2	0.923	.598	1.4
Acetophenone	77.24	0.8528	.752	1.3
Nitromethane	114.8	1.03	.896	1.0
Acetonitrile	173.6	0.7155	.922	1.0
Paraldehyde	62.6	0.873	.675	1.5
Propyl alcohol	162.6	0.736	.833	1.6
Methyl iodide	46.1	2.2146	.390	1.4
p-Cymene	66.3	0.7248	.414	1.5

Summary

The dielectric constants of 35 organic liquids have been determined at the boiling point under a pressure of 760 mm.

A method has been suggested for evaluating the volume occupied by the molecules in the liquid state.

The above idea was applied to Bakker's equation for the latent heat of vaporization.

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