THE DIELECTRIC CONSTANT OF LIQUIDS UNDER HIGH PRESSURE

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Abstract

The dielectric constants of toluene, carbon bisulphide, normal pentane, normal hexane, ethyl ether and iso-amyl alcohol were measured by a capacity bridge using a specially constructed liquid condenser at both 30° and 75°C (22.4°C only for the last liquid), for frequencies of 600,1000 and 2000 cycles per sec. and under pressures from 1 up to 12,000 kg/cm.^{2}. For the first four liquids, the dielectric constant is practically independent of the frequencies used. The values of $\frac{\varepsilon-1}{\varepsilon+2}\cdot\frac{1}{d}$, $\frac{\varepsilon-1}{d}$ and $\frac{\sqrt{\varepsilon}-1}{d}$ were calculated. The first expression was found to be the most nearly constant and always decrease with increasing pressure, by about 3% for toluene and carbon bisulphide 8% for ethyl ether, and 19% for iso-amyl alcohol.

I. Introduction.

The effect of pressure on the dielectric constant of liquids was first investigated by Röntgen[1] in 1894. He found that up to 500 atmospheres, the change of dielectric constant of water and ethyl alcohol was less than 1%. In 1895 Ratz[2] confirmed Röntgen's statement for water and in addition he made observations on ether, benzene, aniline, and amyl alcohol, using pressures up to 250 atmospheres. Their results are more or less qualitative.

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(1) W. C. Röntgen, Wied. Ann. 52, 593 (1894).

(2) F. Ratz, ZS. ph. Chem. 19, 94 (1895).

Working with pressure up to 500 kg./cm^2, Ortvay[3], in 1911, examined nine liquids including ethyl ether, totuene, and carbon disulphide. He found that the dielectric constant at any pressure, within the pressure range used, may be represented by the equation

$$\varepsilon=\varepsilon_o\ (1+\alpha p-\beta p^2) \qquad (1)$$

where ε and ε_o are the dielectric constant, at any and zero pressure respectively, α and β are positive constants being 7.26×10^{-5} and 1.33×10^{-8} respectively for carbon disulphide at 18°.91 C and p is the pressure in kg/cm^2. Falckenberg[4] took up the same problem and measured the dielectric constant of water, ethyl alcohol, methyl alcohol, and acetone, using $\lambda=5$m. and $P=200$ atmospheres. The refraction constants $\frac{n-1}{d}$, $\frac{n^2-1}{d}$, $\frac{n^2-1}{(n^2-2)d}$ were calculated; a good agreement was found for the expression $\frac{n^2-1}{d}$ in case of water and the two alcohols. Waibel[5] measured the dielectric constant of CS$_2$, benzene, hexane and air from 1 to 130 kg/cm^2. An electon tube was used as an exciter and a vibration galvanometer as a detector. His results may be represented by a formula as equaion (1). In 1925, Grenacher[6] published a paper in which he stated that polar liquids were apparently more sensitive to the influence of pressure than non-polar liquids; but the highest pressure used was only 60 atmospheres and no generalization can be drawn from his data. In the same year, appeared Franck's[7] measurements on benzene, hexane, heptane and carbon disulphide at $\lambda=600$m. and pressure up to 800 atmospheres. Kyropoulos[8] published in 1926 his results on the dielectric constant of ethyl ether, carbon disulphide, chloroform, petroleum ether, acetone,

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(3) R. Ortvay, Ann. d. Phys. 36, 1 (1911).
(4) G. Falckenberg, Ann. d. Phys, 61, 145 (1920).
(5) F. Waibel, Ann. d. Phys. 72, 161 (1923).
(6) M. Grenacher, Ann. d. Phys. 77, 138 (1925).
(7) C. Franck, Ann. d. Phys, 77, 159 (1925).
(8) S. Kyropoulos, ZS. f. Phys. 40, 507 (1926).

ethyl alcohol, methyl alcohol, water, pyridine, carbon tetrachloride, and benzene at 20°C, $\lambda=350$m., and pressure up to 3000 kg/cm^2.

From the above practically exhaustive, though brief, review of the previous work on the subject, we see that little work has been done on the pressure effect of the dielectric constant in comparison with the temperature effect which has been intensively studied both theoretically and experimentally. However, as Prof. Bridgman[9] pointed out clearly that "the significance of high pressure as a tool of atomic research lies in the extreme simplicity of the change it produces in the external conditions, merely pushing the atoms closer together so that they are compelled to give a somewhat more intimate account of their own innermost selves. The change produced by pressure are obviously much simpler than those produced by a change of temperature....Further, by combining the effects of temperature and pressure, we extend enormously the field in which we may look for phenomena suggestive for our theories, for the field is now two instead of one dimensional." The pressure effect is simpler than the temperature one, because the kinetic energy due to temperature agitation remains unchanged Moreover, through the researches of Professer Bridgman, we can extend the pressure range greatly. The highest pressure used by the previous observers is 3000 kg/cm^2 (500 kg/cm^2 only at the beginning of the present work) while 12,000 kg$\sqrt{}$cm^2 is the every day practice in Prof. Bridgmen's laboratory. In addition, most theories have been developed for an electrostatic field, while nearly all the measurements on dielectric constants were taken at high frequency, usually $\lambda>10^4$ cm. being denoted by $\lambda=\infty$ in the tables. At the present time, we can measure the dielectric constant precise to at least 1/10% with a capacity bridge at audio frequency say 1000 ~/sec., or $\lambda=3\times10^7$ cm. In view of all these points the present work has been taken.

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(9) P. W. Brigman, Jour. Franklin Inst., Vol. 200, No. 2, p. 148 (1925).

II. Experimental Details.

(A) The Method.

The dielectric constant of liquids was measured, in the present investigation, with a General Radio Capacity Bridge with some modifications. For all the liquids under examination, except ether and iso-amyl alcohol, the capacity of the unknown liquid condenser is given by the difference of two settings of a carefully calibrated precision air condenser. This direct substitution method will eliminate all the errors due to the inequality of the ratio arms and unequal dielectric losses in various parts of the bridge, etc. For ether, the method of measurements is the same but we have to use a quite complicated formula in calculating the unknown capacity at 75°C and a somewhat simpler one at 30°C. The complication came in on account of the large dielectric loss of the liquid condenser. For iso-amyl alcohol, I was forced to use parallel resistances across the two capacity arms of the bridge because the liquid is conducting. Thus the alcohol condenser was replaced by a perfect condenser in parallel with a resistance. This is again a direct substitution method.

(B) The Apparatus.

1. The Liquid Condenser.

In designing the liquid condenser, one must remember that it will go into a high pressure cylinder, thus its dimensions are limited to certain extent; that the liquid under investigation must not mix with the liquid used for transmitting the pressure, i.e., the condenser should have perfectly no mechanical leak at atmospheric pressure as well as under high pressure and at the same time we must have some way to transmit the pressure to the liquid in the condenser; and that it should be easily disassembled for cleaning after every use. The final form of the condenser is shown in Fig. 1. The condenser consisting of two concentric circular cylinders was made of brass. Steel can not be used, because we are going to measure the capacity of this condenser at audio frequencies from 600 ~/sec. to 2000 ~/sec. and at such frequencies the hysteresis loss of the steel will mingle with the dielectric loss of the condenser, thus introducing errors to the results. While brass has the advantage of being easily worked with it is comparatively active chemically with the liquids. However, I found no trouble at all with all the liquids except iso-amyl alcohol. Alcohols have definite chemical reaction on zinc which is about 1/3 in brass. For the alcohol, therefore, we must have the condenser and the reservoir, except

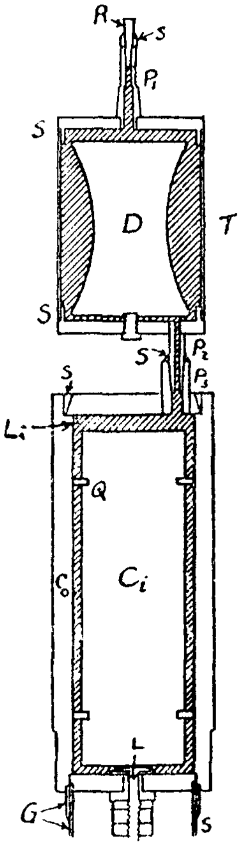

Fig. 1. Liquid condenser and reservoir.

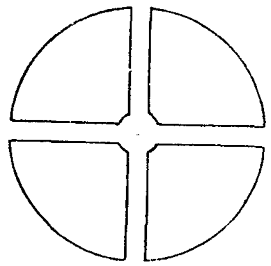

Fig. 2. End view of the Core, *D*.

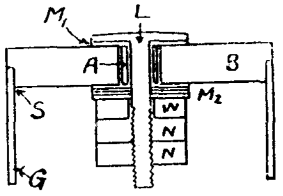

Fig. 3. Bottom of the liquid condenser.

the tin tube, gold-plated. The inner cylinder of the condenser is 1.820 inches (4.622 cm.) long and 0.625 inch (1.587 cm.) in diameter. In order to cut down the capacity of the iso-amyl alcohol condenser within the range of the precision condenser, namely 1500 $\mu\mu$f, a smaller inner cylinder, C_3, made of brass and gold-plated, was constructed, being 1.755 inches (4.456 cm.) long and 0.563 inch (1.428 cm.) in diameter. Near each end of the larger inner cylinder, three quartz pins, Q, (only two shown in Fig. 1 for convenience of drawing), all being 0.078 inch (0.198 cm.) long and the three upper ones 0.052 inch (0.132 cm.) and the three lower ones 0.046 inch (0.117 cm.) in diameter. These pins keep the inner cylinder concentric with the outer one. They should fit the holes in the cylinder very tight and were grinded gradually to the desired length within 0.0005 inch (0.0013 cm.) with an oil stone. This was somewhat tedeous owing to the fact that the small quartz pins were very liable to break. The small inner cylinder was also provided with six quarty pins of slightly different dimensions. The outer cylinder of the condenser, C_O, is 0.850 inch in outside diameter and well fits the high pressure cylinder. Its inside dimensions are 1.883 inches (4.872 cm.) long and 0.656 inch (1.666 cm.) in diameter, thus leaving a space of 0.031 inch (0.079 cm.) and 0.016 inch (0.041 cm.) between the flat surfaces and the curved surface of the outer cylinder and the large inner cylinder respectively. Various details of the construction of the bottom of the condenser require comment as I had much trouble with it. In the first place, the surface of the high potential lead, L, and that of the brass bottom, B, between which there are a few mica washers, should be perfectly flat; otherwise mechanical leak will surely occur right here as was evidenced by the nonrecovery of the capacity of the condenser after an application of pressure. The final scheme adopted was to smooth both surfaces successively on different grade of slates and finally to grind the two surfaces against one another with a little bit of very fine rotten stone powder between them. This method was found to be very satisfactory. In the second place, the mica washers, *M*, baked in a paraffin bath at 130°C for about one or two hours before using, always caused the capacity of the condenser bottom changing from time to time, most probably due to some occluded moisture in the mica. The mica washers used here as well as those for the insulating high pressure plug were contained in a glass tube and cooked in a salt (a mixture of potassium and sodium nitrates having a eutectic point) bath at 400°C for about two hours to drive away the moisture without destroying the crystalline structure of mica. With all these precautions, the capacity of the condenser bottom was entirely constant at the begining and the end of a run or runs. It is evident from the above, that the condenser bottom and the high pressure insulating plug should be kept in a desiccator when they were not in use.

Referring to Fig. 3, we note that the top of the insulating lead, *L*, is slightly convex. The thickness of the mica washers M_1 was about 0.005 inch (0.013 cm.), that of M_2 about 0.040 inch (0.102 cm.). Although it is very desirable to have the capacity of the condenser bottom small in comparison with that of the main condenser by making the mica washers thicker but the question of mechanical leak soon came in. The above mentioned thicknesses for the mica washers were about the limiting values. The diameter of the mica washers and of the top of *L* is 0.250 inch (0.636 cm.). "*A*" is a pipe stone sleeve to keep the stem well insulated; N, N are brass nuts. As given in the tables, mica is less compressible than brass, hence, if the nut is tightened at atmosphere pressure it will be more tight under high pressure. To insure further, a steel washer, *W*, of about 0.060 inch (0.152 cm.) was placed between the lower mica washer and the nut.

The upper part of Fig. 1 is a reservoir designed by Professor Bridgman[10] several years ago for his own research. It consists essentially a tin tube, *T*, soldered on two end discs of brass with a brass core, *D*, having cross-grooves, shown in Fig. 2, at

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(10) P. W. Bridgman, Proc. Amer. Acad., 59, 146-147 (1923).

both ends to facilitate the flow of the liquid, to cut down the unnecessary highly compressible liquid, L_i. In soldering the tin tube to the end discs, it is preferable to use the ordinary solder instead of easily fusible solder which will not stick very well. Since the melting point of the tin reservoir is about the same as that of the solder and since I was not allowed to use any soldering flux (the ordinary soldering fluid, being an alcohol solution and containing some water and glycerine, would impair my result if it were mixed, even in minute quantity, with the liquid under test; solid flux such as rosin will disolve in the liquid, this introducing errors), it took a little practice to do the work satisfactory. The procedure was to tin the end discs well with the aid of soldering fluid, then to clean and wash the discs in petroleum ether, then to heat the disc with a soldering iron until the solder melts, then to put the tin tube on and twist a little bit in such a way as to make the tube sticking on the disc, and finally to have the tube well soldered. Usually I soldered the upper disc on first and had no trouble; and then for the lower disc troubles often came in, possibly due to the larger heat capacity of the core. The reservoir and the condenser, also when these two assembled togather, were always immersed in petroleum ether to test if there were any leak by a hand pump. All the pipes, *P*'s, and the sleeves *G*'s were made of German silver which has a comparatively low heat conductivity and thus makes the soldering processes easier. The joints of pipe to pipe, or rod, *R*, to pipe were cone-shaped and good fit. In the figures, *S* denotes where solder was used. For every liquid, a new tin tube was used and the condenser was disassembled and carefully cleaned. The liquid was filled in vacuum in a way described by Prof. Bridgman[10]. The glass reservoir used in filling had a ground joint with the lower part of the pipe P_1. After filling, the liquid in the pipe P_1 was taken off and the rod, *R*, was put on. In soldering on the rod, a rubber tubing was slipped on the top disc and some petroleum ether was poured in to surround the pipe, otherwise the liquid in the reservoir would boil and push the rod right off.

This is especially important for liquids having low boiling point. In actual use the space between the condenser and the reservoir was filled with a piece of brass in order to cut down the volume compression. The lead, *L*, was connected to the stem of the high pressure insulating plug and forming the high potential terminal of the condenser. The condenser was assembled together with the insulating plug through a joint piece of steel of which the slots were covered with paper to avoid the electrical short-circuit, which occurred several times at first, on account of the falling copper chips from the washers of the moving piston. This precaution together with the use of a filter in the upper high pressure cylinder did get rid of the electrical short-circuit considerably, though not entirely. In passing, I may state that the high pressure insulating plug, having only one lead and being particularly simple, was not put directly in a paraffin bath at 130°C as usually was done but was in a brass container dipped in the bath. The objection to the usual process is that paraffin in the stem when melts off will change the capacity of the plug. The whole outfit was then put into the high pressure cylinder which was immersed in an oil bath. In making or breaking the connection of the liquid condenser to the capacity bridge, a mercury valve, shown in Fig. 4, was used. It was essentially an U-shaped capillary tube of 3/8 inch in outside diameter with a hole of about 1/16 inch. The distance

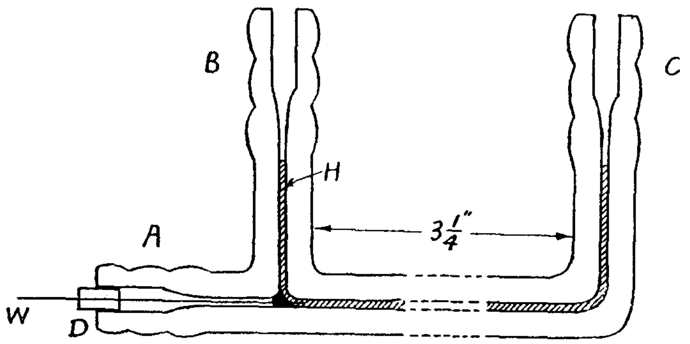

Fig. 4. Mercury Valve.

between *B* and *C* was about 3½ inches. Enlargements were provided at the end of limbs *B* ond *C*, both limbs about 1½ inches long, to avoid the overflow of the mercury, *H*, shown shaded. A tungsten wire, *W*, was sealed in *B* and came out through the glass tube, *A*, 1 inch long, and a cork, *D*. A copper wire connected to the tungsten through a small copper tubing and protected by a rubber tubing slipped and tightened on *A*, was connected to the high potential binding post of one arm of the capacity bridge. *B* was connected to the high pressure plug by a rubber tubing. One end of a 3/8 inch outside diameter capillary glass tube of about 15 inches long was connected to *C* while the other end to a rubber bulb with a rubber tubing. The rubber tubing used was specially manufactured by a rubber company and supposed to stand oil at 75°C. To prevent to certain extent the attack of the oil on the rubber and the swelling of the tubing, all the rubber tubings dipped in the oil bath were covered with several layers of electrical tape. By turning a screw, and thus squeezing or releasing the rubber bulb, outside the bath, of course, electric connection between the liquid condenser and the bridge was made or broken through the mercury thread in *B*. This arrangement has the advantage that the capacity of valve and the copper wire from *A* and out of the bath then to the bridge remained constant since the movement of the mercury thread was less than half a mm. in oder to make or break the contact. This feature is important for accurate measurements.

2. The capacity bridge and accessories.

Much has been said in connection with the liquid condenser, we shall now consider the capacity bridge. A capacity bridge is nothing but a well shielded impedance bridge with two equal resistance ratio arms. Special symmetrical input and telephone transformers with a static shield between primary and secondary are used. But the distributed capacities and the resistances due to the connecting wire as well as that due to the dielectric losses in various arms are not sufficiently equalized and so a direct substitution method should be used for accurate measurements. The bridge used in the present work and the balancing and the precision condenser were all made by the General Radio Company, combridge, Mass. The bridge was modified only in one thing, namely, the ground connection was made at the capacity joint instead of the resistance one. This was necessary, because then we could earth one terminal of the insulating high pressure plug and thus facilitating the manufacturing and saving the troubles of insulation. The bridge was set on a table covered with copper sheet which was well grounded to a water pipe.

The precision condenser was carefully calibrated against another precision condenser of Cruft Laboratory, Harvard University. The latter had been calibrated by absolute measurements, expressing the capacity in terms of time and a standard resistance. Since the condenser settings are by no means proportional to the capacities, it is imperative to calibrate in small intervals and tabulate the results. The capacity difference of two settings must be, therefore, obtained from the calibration table instead of simple subtraction of the direct readings. Two hundred and fifty one points were calibrated for the whole range of the precision condenser, about 1500 $\mu\mu$f. (micro-micro-farads). Main and interpolation tables were constructed.

Under the supervision of Prof. R. F. Field, a variable audio frequency oscillator, a two stage amplifier and a decade high resistance box of a total resistance 100,000 ohms were specially made for the present work.

The frequency of the oscillator ranges from 250 to 4,500 cycles per second, although only three frequencies, namely 600, 1000 and 2000 cycles per second, were here used. The tube used was a 7.5 watts power tube. It is well known that the frequency from a vacuum tube changes considerably with many factors, notably the filament current. The oscillator was calibrated under the actual load with an audio-frequency-meter of Cruft Laboratory. It was found the frequency did change with time and for filament current varying from 1.20 to 1.25 amperes.

With a step-down transformer, from 110 volts to 7.5 volts, the 110-V. A.C. was used for heating the filament. The filament current was always adjusted with a rheostat to little more than 1.20 amperes before every set of measurements was taken. The plate voltage was about 330 volts from a set of 400 volts storage batteries. With the above mentioned precautions, the frequencies were accurate within 1/10 per cent. The output voltage at any frequency used was adjusted by merely changing the coupling between the oscillatory and output coils to about 30 volts. The oscillator was placed in another room to avoid its direction action on the bridge and also the disturbing sound. The wires (Flexible Conduit) connecting the oscillator to the bridge were well shielded to cut off any disturbing oscillation such as another oscillator in the building. Without going further to the details and many practical difficulties in construction, it suffices to state here that the oscillator served for the present work satisfactorily.

The two-stage audio-amplifier consisted mainly two Audio-Transformers (G.R.Co.), two Radiotron UV-199 (Radio Corporation of America) and three filament-control-jacks so that the telephone may be connected either directly to the bridge or to one or two stage of the amplifier by simply thrusting the telephone plug in the respective jack. These amplifying units togather with three dry cells to light the tubes, one large block of 45 volts plate batteries, a rheostat and a voltmeter for adjusting the filament voltage to about 3 volts were all contained in the same box. The amplifican for one stage is about 15.

In measuring ether and iso-amyl alcohol, a high resistance box was necessary. It was made of twenty 5000-ohm Cards (G.R.Co.) and eleven contact switches and is a 10-step decade resistance box. It has one special feature, namely, any resistance not in use is entirely disconnected from the bridge circuit unlike the ordinary resistance boxes for which the resistances are always hanging on the circuit and thus introducing errors to the capacity measurements due to thir own capacity and their capacity to the ground.

The balancing point of the bridge was detected by a Western Electric Double Head Telephone Receiver. It is most sensitive to a frequency of about 1000 cycles per second since its diaphram has a natural frequency below and near that frequency. If we use 500 cycles per second alternating current to excite the bridge, then near balance, the fundamental is faint while the first harmonic, being very sensitive to the telephone, is so prominant that a perfect balance of the fundamental is extremely hard to detect. For this reason, frequency of 600 cycles per second in place of 500 cycles per second was used. Even for 600 cycles per second the measurements are difficult without any other device to eliminate the harmonics. An electric filter suggested itself at first; but it was found finally that a tuning condenser connected to the two binding posts of the bridge marked telephone, was the simplest and also the best method. With this condenser, we can tune the whole bridge circuit to a desired frequency. It was measured on a vacuum tube voltmeter that after tuning the bridge circuit to 600 cycles per second, then the voltage of 1200 cycles per second across the telephone, if the telephone was connected directly to the bridge or to one-stage amplifier, was reduced to only 1/10 or 1/50 respectively of the voltage which would be impressed on the telephone without tuning. Therefore by this simple device, we can eliminate the trouble of harmonics. For 600 cycles per second, the tuning capacity was 0.033 or 0.019 micro-farad according to whether the telephone was connected directly to the bridge or to 1-stage amplifier.

3. High pressure producing and measuring outfits.

In this connection, the reader is invited to consult Prof. Bridgman's several papers among which two are most important, namely, "The Measurement of Hydrostatic Pressure up to 20,000 kg/cm^2."[11] and "The Technique of High Pressure Experimenting."[12] However, it is nearly a practical impossibility for any

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(11) P. W. Bridgman, Proc. Amer. Acad., 47, 321 (1911).

(12) P. W. Bridgman, Proc. Amer. Acad., 49, 627 (1914).

body to describe the expermental details and difficulties in any completeness. One can not expect to acquire the technique of high pressure researches by simply reading; but through reading, one can get a general idea.

The pressures were measured with a manganin resistance gauge. It has been shown by Prof. Bridgman[11] that the pressure up to 13,000 kg/cm^2 is directly proportional to the change of resistance produced by it. This relation makes the calibration of the gauge particularly simple. What one has to do is then to measure the resistance of the manganin coil at two known pressures. Atmospheric pressure and the freezing pressure of mercury at 0°.0C (7640 kg/cm^2.)[13] were chosen as the two fixed points. A special lower high pressure cylinder with a steel cup containing about 100 grams of mercury was used. The cylinder was completely immersed in a well stirred ice-water bath. The change of resistance of the manganin coil was measured on a previously calibrated Carey Foster bridge. During freezing, the volume of mercury decreased by about 3.3% While the pressure remained constant. Two sets of readings were made and gave the same result. For each set, two readings on the bridge were taken, one with increasing and the other with decreasing pressure and differed from one another less than 3/10 mm. corresponding to a pressure of about 7 kg/cm^2. Care should be taken to have enough solid mercury to show up the volume change; but do not let all the mercury freeze. At 17°.0C and atmospheric pressure the resistance of the manganin coil was found to be 116.38 ohms and at 17°.0C, the change of resistance due to pressure from 1 to 7640 kg/cm^2. was 2.072 ohms. The pressure coefficient at 17°.0C is, therefore, 2.331×10^{-6} which has been used in all the calculations of the pressures. The temperature correction for the pressure coefficient within the range 0°-50°C is only about 1 in 20,000 per degree[14] and

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(13) P. W. Bridgman, Proc. Amer. Acad., 47, 423 (1911).

(14) Reference 11, p. 339.

therefore neglibible. The accuracy of the readings[15] with the manganin gauge is at least 1/10 per cent at 8,000 kg/cm².

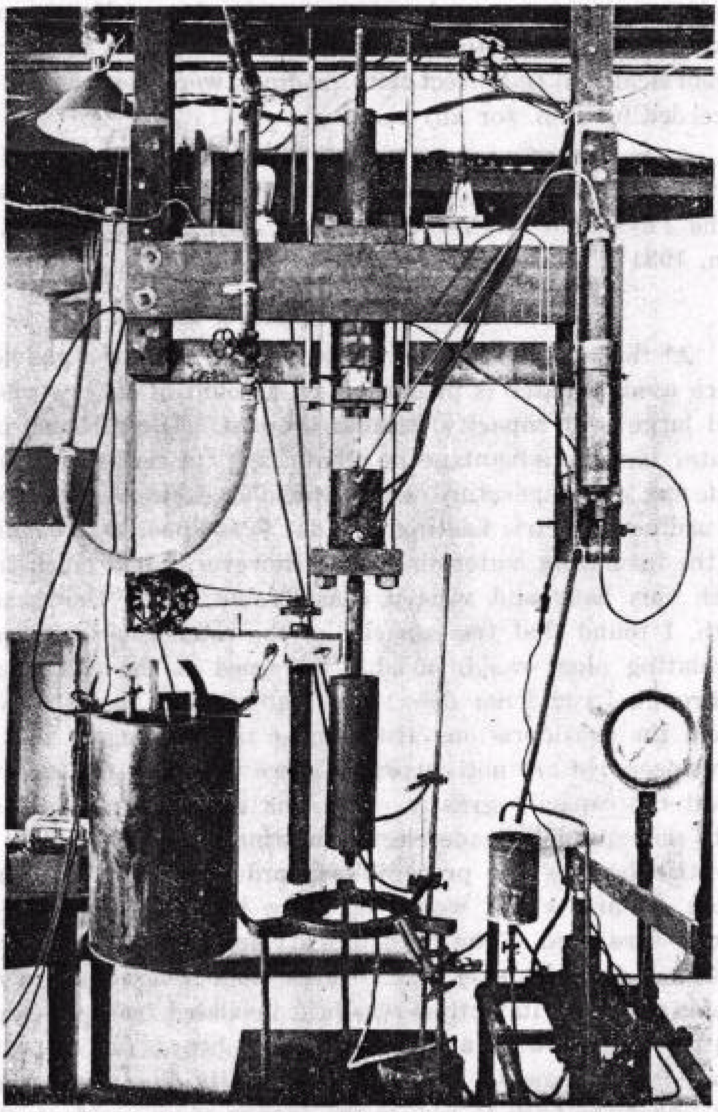

Plate 1—Photograph of a typical high-pressure installation.

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(15) Reference 11, p. 342.

As mentioned above, the pressures were measured indirectly on a Carey Foster bridge. The bridge wire was calibrated against a set of standard resistances (Leeds and Northrup Co.) and was found pratically uniform. Corrections to be added algebraically to the direct wire readings were plotted and never exceeded 0.4 mm. for any reading.

A photograph of a typical high-pressure installation is shown in Plate I, taken from Prof. P. W. Bridgman's book on "The Physics of High Pressure" (G. Bell and Sons, Ltd., London, 1931).

4. Temperature regulating Device.

At the beginning of the work, a water bath and gas heaters were used. Water is preferable on account of its low viscosity and large heat capacity, besides the cost. Direct flame of gas heater has the advantage of eliminating, to certain extent, the time lag of temperature which would be conceivable if we use an ordinary electric heating unit due to the poor heat conduction of the insulating materials used. However, I had much trouble with this bath and wasted considerable time. Using such a bath, I found that the capacity of the condenser including the insulating plug was invariably increased at the end of a run althrough I could not detect any water leaked into the system. From the considerations given under the heading of the liquid condenser, we are not surprised, since traces of moisure would affect the capacity greatly. For this reason, a cotton seed oil bath and specially made electric heating coils were finally used. Electric heaters are preferable in order to avoid the possible catch of fire which would be more liable to happen if gas flame were used. The bath has a volume of about 11 gallons (2470 cu.ft.); its side was covered with several layers of asbestos cloth and its bottom was heat insulated from the supporting iron stand with a piece of primer board (a composite of asbestos and cement). A large tank partly filled with sand was put under the bath to reduce the danger of an accident, though never happened during the entire course. Since the oil is more viscous than water, two stirrers were necessary.

The heating coils were made of bare Nicvome wire, having a resistance of 3.79 ohms per foot. The wire was wound on a frame of primer board, about 12 inches long and 6 inches wide. Each coil had 14 turns (28 feet). One coil was tapped at the 5th and the 11th turn while the other just at the middle. The coils were completely immersed in the oil, while all the binding posts were outside the bath so change of connections could be easily made. 110-volt D.C. from batteries was used, for the 60 cycles per second 110-volt A.C. and the noise from a 110-V D.C. generator would prevent to detect an accurate balance of the capacity bridge with a telephone. A 11-turn coil connected to the source would about, but not quite, maintain the bath at 75°C; and two 7-turn coils were used to raise the temperature. For 30°C, no constant heating coil was necessary, only a 11-turn coil was used to compensate the fall of temperature. The current through the coil, used for raising the temperature of the bath, was thrown on or cut off automatically with the aid of a system of mercury regulator and vacuum tube relay.

A mercury regulator is essentially a glass U-tube of about 10 inches high and ½ inch in diameter, closed at one end and provided with a glass capillary tube and an enlargement at the top of the other end. A platinum or tungsten wire was sealed in the U-tube near and below the capillary tube. The regulator was filled with clean mercury to such an extent that at the desired temperature, the mercury will come up to the middle of the capillary tube. Electric connection was made when the mercury thread was raised to such a height that it was in contact with the platinum needle. The whole thing was mounted on a brass frame. The U-tube was entirely immersed in the oil. Two such regulators were used, one adjusted for 30°C and the other for 75°C. With these regulators, we can easily adjust the temperature of the bath to ±1/20°C and under favorable conditions to ±1/30°C.

The cheif trouble with such a regulator is the poor contact due to the oxidation of the mercury, caused by the electric sparks when the circuit being broken. To eliminate this, a vacuum tube relay was used. In this relay, the mercury regulator was connected to the grid and the filament negative of an electron tbue. Since the grid voltage is low and the grid current is extremely small, there will be practically no spark across the platinum needle and the mercury thread when the contact is broken. Proper grid leak circuit should be provided for. The relay circuit which operated the switch for the heating current was connected to the plate and the filament positive. Four 120-Watt carbon lamps were connected between the positive terminal of 110-V. D.C. and the filament positive and a 75-Watt tungsten lamp was connected between the filament negative and the negative terminal of the source. The purpose of these lamps is to adjust the voltage across the filament to about 3.5 volts and to polarize the grid negatively with respect to the filament negative. The whole system may thus be operated by a 110-V. D.C. source. When the mercury regulater circuit was broken, the plate current was about 1 M.A. and when the curcuit was closed, the grid having a higher potential than before and being at the same potential as the filament negative, the plate current was increased to 10 M.A. which is large enough to operate the switch.

(C) General Procedure.

For all the capacity measurements, sets of readings were always taken at pressures in the order of 1,000, 3,000, 5,000, 8,000, 12,000, 10,000, 6,500, 4,000, 2,000, 500, 150 kg/cm^2. approximately and sometimes at atmospheric pressure as the last one. For toluene and normal-hexane at 30°C, the highest pressures used were 9,500 and 10,000 kg/cm^2. respectively which are pretty close to their freezing pressure. Since at atmospheric pressure the boiling point of CS_2, N-pentane, N-hexane and Ethyl ether is lower than 75°C, it is evident that for the 75°C runs, measurements cannot be taken for such liquids at pressures lower than 150 kg/cm^2., say. In such cases, the lowest pressure used varys from 150 to 500 kg/cm^2.

and will be recorded for each liquid. The pressure of 1000 kg/cm^2. was chosen as the first reading' because this pressure seemed to be high enough to give the apparatus a good set, for example, the stem of the insulating plug, whence better results could be obtained. The idea of taking readings at increasing and decreasing pressures was to check up whether any transmitting liquid had leaked into the condenser. In a few occasions, same foreign liquids got into the condenser when the pressure was lowered and the points for increasing and decreasing pressures laid on two different smooth curves. As my experience goes, leak occurred much more often for the decreasing pressures, especially for the steps 12,000-10,000-6,500 kg/cm.^{2}.

The pressures were measured on a Carey Foster bridge bath before and after the capacity measurements. Two readings were taken each time and after reversing the switch, two more; thus eight readings were taken for each pressure. At every pressure capacity measurements were made for three frequencies, 600, 1000 and 2000 cycles per second. For every frequency, four and two readings were taken when the liquid condenser was connected in and disconnected from the bridge respectively. The zero readings, i.e. when the liquid condensesr was disconnected, were found practically constant throughout the whole run and, therefore, two except the first set for which also four zero readings for every frequency and every pressure were considered to be good enough. In order to get a perfect silence in the telephone, the resistance should, of course, be also balanced. This resistance was taken down every time. Time was recorded after every measurement of pressure and of capacity for every frequency. This enables us to make pressure corrections, by interpolation, if there were any change in pressure during the capacity measurements. The temperature of the oil bath was taken after the capacity measurement for every frequency. The total time required for taking all these readings, including the time for changing the frequency of the oscillator, was from 12 to 18 minutes.

(D) Choice and Description of the Liquids.

The most interesting liquids to be investigated are perhaps those having permanent molecular dipoles or polar molecules as called by the chemists. The temperature effect of these dipole liquids can not be explained by the Loretz-Lorenz equation and for this reason, Debye[16] has developed his "dipole theory" to account for the enormous change of dielectric constant with temperature. In the original list a number of the dipole liquids were included; but owing to their conductivity only Ethyl Ether and Iso-amyl alcohol have been measured.

At ordinary temperatures, many of the liquids freeze at low pressure and therefore are not suitable for the present work. Toluene has been chosen as the representative of the ring compounds, because it can stand much higher pressure without freezing than the first member of the family, namely, benzene.

Carbon bisulphide was selected partly because its dielectric constant together with the temperature and the pressure effect had been closely examined and partly for it represents a type of molecule having double bonds.

Normal Pentane and Normal Hexane were used to represent the paraffins, or saturated hydrocarbons.

Iso-amyl Alcohol was from Kahlbaum. It boils from 128°-132°C and is free from pyridine as given by the manufacturer. Both Toluene and Normal Hexane came from Eastman Kodak Company. Their specification are that the toluene is free from sulphur and boils from 109°.5 to 11°.5 C. and that the normal hexane was manufactured synthetically and boils from 68° to 69°C .

The Carbon bisulphide, Normal Pentane, and Ethyl Ether were all prepared by Prof .Keyes of M.I.T. for Prof. Bridgman. The Ether was freshly purified and sealed in a colored glass tube. The carbon bisulphide, sealed in a colored glass container, and the normal pentane, sealed in a glass receptacle, were used before by Prof. Bridgman. All these three liquids

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(16) P. Debye, Phys. ZS., 13, 97 (1912).

are of the highest purity obtainable and their freezing points may be used as standards in thermometry. The freezing points, given by Prof. Keyes[17], are -112°.97 C for carbon disulphide and -123°.40 and -115°.9 C for the first and the second modification of ether respectively.

III. Computation and Results.

(A) Capacity Bridge Circuits.

For all liquids measured, except iso-amyl alcohol, the bridge circuit may be sketched as in Fig. 5. Here R_1 and R_2 are two 5,000-ohm resistances and form the ratio arms of the bridge. C_0 and R_0 denote the capacity and its associated dielectric loss and the resistance of the plates, leads, etc. of the precision condenser including the specially made mercury valve previously described. The liquid condenser including the insulating plug is represented by C and R for its capacity and dielectric loss. The liquid and the precision condenser were connected in parallel, forming "A"-arm of the bridge, and were balanced by a

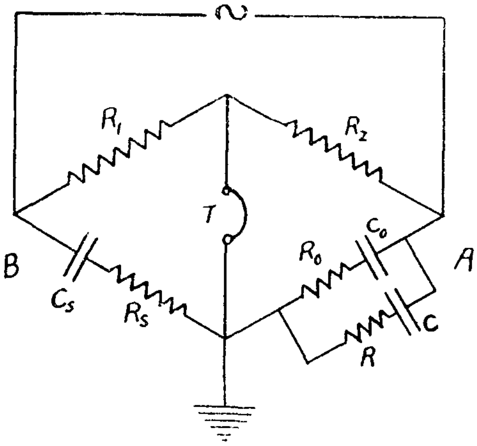

Fig. 5. Bridge Circuit for measuring all liquids except alcohol.

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(17) F. G. Keyes, Townshed and Young, Jour. Math. and Phys.; M.I.T., I, 308 (1922).

condenser C_s and a resistance R_s in the "B"-arm. Since the ratio arms were carefully adjusted for their equality, we shall assume that they are equal. This assumption will not affect the final results, expect for ether at 75°C, because direct substitution method has been used. We shall further denote the capacitance of the condensers by X with corresponding subscript. Equating the impedances of the A and B-arms, we have

$$\frac{(R+iX)\ (R_o+iX_o)}{(R+R_o)+i\,(X+X_o)}=R_s+i\,X_s$$

Separating the real and the imaginary part,

$$X_s=\frac{(R+R_o)\,(RX_o+R_oX)-(X+X_o)\,(RR_o-XX_o)}{(R+R_o)^2+(X+X_o)^2} \qquad (1)$$

$$R_s=\frac{(R+R_o)\,(RR_o-XX_o)+(X+X_o)\,(RX_o+R_oX)}{(R+R_o)^2+(X+X_o)^2} \qquad (2)$$

Since the R's are negligible in comparison with the X's, except for ether, these two equations reduce to

$$X_s=\frac{XX_o}{X_o+X}, \qquad \text{or} \qquad C=C_s-C_o \qquad (3)$$

$$R_s=\left(\frac{X_o}{X_o+X}\right)^2R-\left(\frac{X}{X_o+X}\right)^2R_o\doteq\left(\frac{X_o}{X_o+X}\right)^2R,$$

or $$R=\left(\frac{C_s}{C}\right)^2R_s \qquad (4)$$

where C_s and C_o are the capacities of the precision condenser when the liquid condenser is in and out respectively, and R_s may be read directly on the bridge. In case of Toluene, Carbon Bisulphide, Normal Pentane, and Normal Hexane, therefore, the capacity of the liquid condenser is given by the difference of two precision condenser settings and the precision obtained is independent of the bridge itself. In passing, it may be stated here that C_s was always nearly equal to 1,000 micro-micro-farads.

Returing now to the general equations (1) and (2), we get, by performing the formal algebraic processes,

$$X=\frac{1}{2\alpha}\left\{-\beta\pm\sqrt{\beta^2-4\alpha\gamma}\right\} \qquad (5)$$

$$R=\frac{1}{2\alpha'}\left\{-\beta' \pm\sqrt{\beta'^2-4\,\alpha'\,\gamma'}\right\} \tag{6}$$

where $\alpha\equiv 1+\left(\frac{\alpha_1-\alpha_2}{\beta_2-\beta_1}\right)^2,$

$$\beta\equiv\alpha_1+\frac{2(\alpha_1-\alpha_2)(\gamma_1-\gamma_2)}{(\beta_2-\beta_1)^2}+\frac{\beta_1(\alpha_1-\alpha_2)}{\beta_2-\beta_1},$$

$$\gamma\equiv\gamma_1+\left(\frac{\gamma_1-\gamma_2}{\beta_2-\beta_1}\right)^2+\frac{\beta_1(\gamma_1-\gamma_2)}{\beta_2-\beta_1};$$

and, in turn, $\alpha_1\equiv\frac{2\,R_sX_o}{R_s-R_o}$, $\beta_1\equiv-\frac{X_o^2+R_o^2-2\,R_sR_o}{R_s-R_o}$,

$$\gamma_1\equiv-\frac{R_s(X_o^2+R_o^2)}{R_s-R_o}\qquad \alpha_2\equiv-\frac{X_o^2+R_o^2-2\,X_sX_o}{X_s-X_o},$$

$$\beta_2\equiv\frac{2\,X_sR_o}{X_s-X_o}\qquad \gamma_2\equiv\frac{X_s(X_o^2+R_o^2)}{X_s-X_o}.$$

α' β' and γ' may be obtained from α, β, and γ by simply interchanging α_1, α_2 and β_1, β_2.

Equation (5) used in calculating the capacity of the ether condenser at 75°C and under various pressures up to 12,000 kg/cm^2.

In view of the relative magnitudes of R's and X's, the capacity of the ether condenser at 30°C an be calculated by the following much simpler formula (8). Accurate to the fifth figure, we may rewrite (1) in the form of

$$X_s=\frac{R^2X_o+XX_o(X+X_o)}{R^2+(X+X_o)^2}=\frac{X_oX}{X+X_o}\left\{\frac{1+\frac{R^2}{X(X+X_o)}}{1+\left(\frac{R}{X+X_o}\right)^2}\right\}$$

Now since $\left(\frac{R}{X+X_o}\right)^2$, denoted by ϱ, was a quantity of a few thousandths, we may expand the denominator into a power series and neglect all terms in $\frac{R}{X+X_o}$ of power high than the fourth, then

$$X_s=\frac{XX_o}{X+X_o}(1+\sigma)$$

where $\sigma=\frac{X_o}{X}\varrho\,(1-\varrho)$

whence $$C=(C_s-C_o)-\sigma C_s \tag{8}$$

where $(C_s - C_o)$ is just the difference of two precision condenser settings and was greater than 256 $\mu\mu$f, while σC_s was less than 3 $\mu\mu$f. We may, therefore, use the approximate values of X and R calculated from (3) and (4) in evaluating σ.

In measuring the dielectric constant of iso-amyl alcohol, the bridge circuit was entirely different from that shown in Fig. 5. The following diagram will show the general connections. The same notations are used here as in Fig. 5, but R_o and R_s are now in parallel with the condensers and their arrow-headed end may be disconnected by removing a stiff copper wire from a small mercury well in a paraffin block. The movement of the wire was so slight that no appreciable error would be introduced on that account.

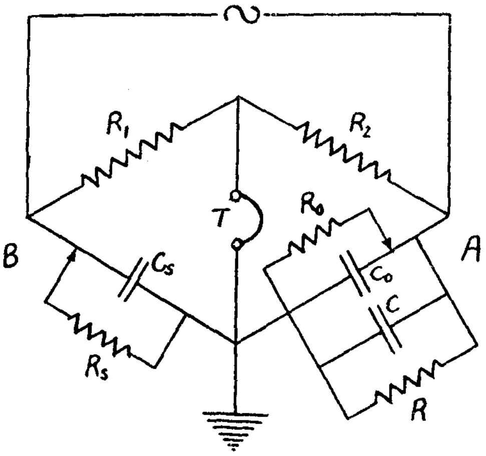

Fig. 6. Bridge Circuit for measuring iso-amyl alcohol.

With the alcohol condenser in A-arm and R_o disconnected, balance the bridge by adjusting R_s and C_o. Leaving the "B"-arm unchanged, disconnecting the alcohol condenser, and connecting R_o in the "A"-arm, rebalance the bridge by adjusting C_o and R_o. Evidently, the difference of the two precision condenser settings and R_o give the capacity and the equivalent parallel resistance of the alcohol condenser. Thus

$$C = C'_o - C_o \tag{9}$$

$$R = R_o. \tag{10}$$

Here again, the precision is independent of the bridge itself. The cheif trouble with this method is that the distributed capacity of R_o can hardly be accurately measured. This will be discussed later on.

(B) Various Corrections.

(1) Capacity of the Insulating Plug and the Bottom of the Liquid Condenser. This capacity together with the liquid condenser proper had been measured on the capacity bridge in a way described above. It is evident that it should be subtracted from the reading obtained. This capacity was about 30 micro-micro-farads while the geometrical capacity of the liquid condenser, i.e., the capacity of the condenser with vacuum as dielectric, was a little over 50 micro-micro-farads and the dielectric of the liquids measured, except iso-amyl alcohol, varies from 2 to 4. It is, therefore, necessary to measure this capacity in the same way, except the inner cylinder of the liquid condenser being replaced by a glass one to cut down the unnecessary highly compressible liquid, at the same temperatures and pressures as that of the liquid condenser. This capacity was neither perfectly reproduciable nor changing regularly, mainly due to the rubber washer in the insulating plug. If the rubber washer were packed more tight then the stem of the insulating plug would go further into the hole, thus making the capacity of the plug larger. Fortunately, the change was found to be small. The same plug and the same condenser bottom were used throughout, except for iso-amyl alcohol. Six runs at 30°C and four runs at 75°C were successfully made to measure this capacity. The average difference between the readings of two successive runs at any corresponding pressure, except at atmospheric pressure, for which the difference was somewhat larger, was 0.3 micro-micro-farad for 30°C and 0.2 micro-micro-farad

for 75°C, while the limit of measurement was about 0.1 micro-micro-farad. The capacity of the plug and condenser bottom was measured before and after the principal measurements of the liquid condenser. The average value of the two runs at the corresponding pressure was used in computation. In this way, the error due to the irreproducibility of this capacity is seen to be nearly within the limit of accuracy of the capacity bridge. The average change of this capacity from 250 to 12,000 kg/cm^2. was 1.0 micro-micro-farad for 30°C and 0.8 micro-micro-farad for 75°C. and is evidently very small.

Before passing, one point deserves to be mentioned here. The capacity of the plug and the condenser bottom at any pressure was found to be greater at 75°C than at 30°C., the average difference being 2.6 micro-micro-farad. At first sight, this seems to be contradictory to what we expect, for the temperature coefficient of dielectric constant is always negative. The change of dimensions due to temperature is inadequate to offer an explanation for such a comparitively large change in capacity, although it might have contributed some. It will be explained later that any condenser may be represented by a dielectric condenser in parallel with an electrolytic one due to electric conduction. The electrolytic capacity is surely larger at 75°C than at 30°C. What we observed is just the net result of several effects, namely the change of electric conductivity, of dielectric constant, as well as of dimensions of the apparatus.

(2) Geometrical Capacity of the Condenser. In order to get the dielectric constant of the liquid we must know the geometrical capacity of the condenser at that temperature and pressure. The capacity of the large liquid condenser, that is, the condenser with the large inner cylinder, with which all the measurements were made, except iso-amyl alcohol, when filled with air at an average temperature of 22°.5C and an average pressure of 76°.7cm. of mercury was measured at the beginning, the middle, and the end of the entire course. Three frequencies, 600, 1000 and 2000 cycles per second, were used every time and for every frequency four readings were taken. The capa-

city, as we expected, did not change with frequencies. All the 36 readings were pratically same, entirely within the experimental error. The average value was 54.03 micro-micro-farads. The capacity due to the six quartz pins with the dimensions given under the heading of the liquid condenser was calculated and found to be 0.15 micro-micro-farad. The capacity of the large condenser, filled with air under the conditions mentioned above, excluding the quartz pins capacity, is then 53.87 micro-micro-farads. Using the value of 1.00059 as the dielectric constant of air at 0°C. and 1 atmosphere, assuming ε-1 being proportional to the density, we can calculate the dielectric constant of air at 22°.5C and 76.7 cm. of mercury. This is 1.00055. Therefore the geometrical capacity of the large condenser at 22°.5C and 1 kg/cm^2 is 53.84 micro-micro-farads.

(3) Temperature Correction for the Condenser. We shall call L_o, the length; D_o and d_o, the inner diameter of the outer cylinder and the diameter of the inner cylinder respectively; and l_o, the distance between the flat surfaces of the cylinders at the top or the bottom of the condenser at O°C. Then at any temperature the capacity of this condenser is approximately equal to

$$C=\left(\frac{L_o}{2\log_e\frac{D_o}{d_o}}+\frac{D_o^2}{8l_o}\right)(1+\alpha t)=C_o+C_o\,\alpha t$$

where α is the temperature coefficient of linear expansion, being 1.88×10^{-5} for brass, t the temperature in degree centigrade. C_o is about 54 micro-micro-farads for our condenser and the correction term $C_o\,\alpha t$ may thus be calculated. The geometrical capacity of the large condenser C_g, at atmospheric pressure is therefore, 53.85 micro-micro-farads for 30°C and 53.89 micro-micro-farads for 75°C. These two values will be used in all the following computations, expect for the alcohol.

(4) Pressure Correction. Let C_p and C_1 be the capacity of our condenser under pressure of p and 1 kg/cm^2 respectively. Then, it can be easily shown that, if β is the linear compressibility,

$$C_p = C_1\ (1-\beta p)$$

or

$$C_1 = C_p\ (1+\beta p)$$

The initial volume compressibility of brass[18] is 8.9×10^{-7} reciprocal megbars. We shall call 2.8×10^{-7} cm^2/kg as the average linear compressibility for brass over the range from 1 to 12,000 kg/cm^2 βp was plotted against p, the curve is, of course, simply a straight line. C_p was obtained from the bridge measurement after properly corrected. We can thus calculate C_1. The ratio of C_1 over the geometrical capacity of the condenser gives us the dielectric constant of the liquid at the given temperature and pressure.

(5) Quartz Pin Correction. As mentioned above, the capacity due to the six quartz pins was calculated to be 0.15 micro-micro-farad. This small capacity will be considered constant and subtracted every time from the capacity of the liquid condenser.

(5) Correction for Eccentricity. As mentioned before, the inner cylinder of the liquid condenser was kept concentric with the outer one with six quartz pins. Now it is interesting to calculate the change of capacity due to the inner cylinder being displaced out of center (Fig. 7).

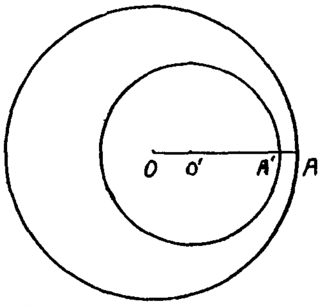

Fig. 7. Eccentric Cylindrical Condenser.

We shall denote the radius of the outer and the inner cylinder by $R = o\text{A}$ and $r = o'\text{A}'$ respectively, the distance between the axes of the cylinders by d and the geometrical capacity of this eccentric cylindrical condenser per unit length by C. Then it can be easily shown that

$$\frac{1}{C} = 2\log_e \frac{R^2+r^2-d^2+\sqrt{\{(R+r)^2-d^2\}\{(R-r)^2-d^2\}}}{2Rr}$$

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(18) Adams, Williamson, Johnston, J. Am. Ch. Soc., 41, 39 (1919).

If d=o, that is, the two cylinders are concentric or coaxial, then the above equation reduces to

$$\frac{1}{C_o}=2\,log_e\frac{R}{r}$$

where C_0 denotes the value of C when d=o.

Now the volume compressibilities are 2.7×10^{-6} and 0.89×10^{-6} for quartz and brass respectively. Whence their linear compressibilities are equal to 0.90×10^{-6} and 0.30×10^{-6} approximately. The length of quartz pin was about 5/64 inch. At 12,000 kg/cm^2 the relative shrinkage of the quartz pin and brass is 5.6×10^{-4} inch.

Assuming that the quartz pins fit tightly the outer cylinder at atmospheric pressure, the maximum value of d at 12,000 kg/cm^2 is about 0.0005 inch. For our condenser, $R=41/128$ inch and $r=5/16$ inch. The maximum error due to the eccentricity of the cylinders is about 2/10%. However, since the capacity of the liquid condenser at the beginning and the end of a run was always found to be practically the same, there is no reason to suspect that the inner cylinder was displaced out of center.

(C) Numerical Results and Comparison with Previous Data.

We shall now give the results obtained for all the liquids investigated. These include the dielectric constant of the liquid at two temperatures, three frequencies, and various pressures. The pressures actually used were not round numbers, as 1,000, 2,000, etc., but they were always adjusted as close as possible so that their differences and hence the corrections for the capacities were very small. Correctoins were made by interpolation, assuming the relation was linear.

If the density, d, of the liquid at various pressures is known, then the Clausius-Mosotti's expression, $\frac{\varepsilon-1}{\varepsilon+2}\cdot\frac{1}{d}$, as well as the Boltzmann's, $\frac{\varepsilon-1}{d}$, were calculated for various pressures. Gladstone and Dale's expression, $\frac{\sqrt{\Sigma}-1}{d}$, will also be given. In these calculations, the dielectric constants at 2000 cycles per second were used.

The geometrical capacity of the condenser at atmospheric pressure and 30°C or 75°C will be denoted by C_g and given at the top of every table. The dielectric constant, ε, was obtained by dividing the corrected capacity of the liquid condenser by this geometrical capacity.

The average temperature coefficient of ε denoted by $\bar{\alpha}$, over the range of 30° to 75°C and at atmospheric pressure and the average pressure coefficient of ε, denoted by $\bar{\beta}$, at two temperatures and various pressure ranges were calculated and compared with the results obtained by previous observers.

The average value was taken in the following way:

$$\bar{\alpha}=\frac{1}{t_2-t_1}\int_{t_1}^{t_2}\alpha dt=\frac{1}{t_2-t_1}\int_{t_1}^{t_2}\frac{1}{\varepsilon}\frac{d\varepsilon}{dt}dt=-\frac{1}{t_2-t_1}log_e\frac{\varepsilon_1}{\varepsilon_2}=-\frac{2.303}{t_2-t_1}log_{10}\frac{\varepsilon_1}{\varepsilon_2}.$$

similarly, $\bar{\beta}=\frac{2.303}{p_2-p_1}log_{10}\frac{\varepsilon_2}{\varepsilon_1}$

All values of $\bar{\alpha}$ and $\bar{\beta}$, including those obtained from the data of the previous observers, were calculated by these two equations.

The dielectric loss of the liquid condenser, represented by an equivalent series or parallel resistance will not be given here, except for ether at 75°C, for two reasons. In the first place, the dielectric loss of the liquid condenser proper was only a small part, say ¼, except for ether and alcohol, of the total loss directly measured and the loss of the condenser bottom and the plug was very sensitive to the moisture in air, the liquids transmitting the pressure, as well as the liquid under examination. Secondly, the values of total loss plotted against pressure did not lie on a smooth curve, those for the decreasing pressures being usually larger. It will suffice to state here that for all the liquids measured, the dielectric loss was invariably decreasing with increasing pressure, except ether at 75°C. The possible explanation is that since under high pressure, the viscosity of the liquid increases rapidly as shown by Prof. Bridgman[19]. The permanent dipoles vibrate in a more viscous medium and the conducting particles, say ions, move with much more difficulty with the result of a decrease in conduction and thus the dielectric loss is decreased. Gyement[20] assumed that liquid contains spherical water particles which, when subjected to an electric field, are polarized and distorted into an ellipsoidal shape, there is thus a displacement current of ions or electrons in the liquid. In the case on iso-amyl alcohol, the ions of the alcohol itself are surely also present. For such low frequency as 600∼/sec. there is, with little doubt, a conduction current through the alcohol or other liquids.

In all the following tables, the percent change of a quantity, its value at the highest pressure minus that at the lowest pressure divided by the latter and multiplied by 100, will be given in the last line under the respective quantity.

Among the liquids measured, toluene was used in all the preliminary experiments and was the first one for the final readings.

(1) Toluene. With some difficulties in the high pressure press and the mercury valve, the measurements were finally accomplished with the same filling for both temperatures. As given by the previous observers, the temperature coefficient of the dielectric constant of toluene is large and so the temperature of the bath was carefully adjusted, being ±1°/30C for C0°C and ±1°/20 for 75°C. This liquid freezes[21] at 9900 kg/cm.^{2} at 30°, so the highest pressure used at 30°C was about 9,500 kg/cm.^{2}. The density, *d*, of the liquid at 30°C and various pressures was taken from Prof. Bridgman's experimental data, the volume of 1 gram of toluene at 30°C and 1 kg/cm.^{2} being assumed 1.166cc.

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(19) P. W. Bridgman, Proc. Amer. Acad., 61, 57 (1926).

(20) A. Gyement, Phys. ZS., 26, 686 (1925).

(21) P. W. Bridgman, Proc. Amer. Acad., 59, 158, table I (1923).

Table I.

Toluene at $30 \pm \frac{1}{30}$ C.

$C_g = 53.85 \mu\mu f$. Pressure used: Lowest = 1 kg/cm.^{2}
Highest=9,463 kg/cm.^{2}

ε at 2000~/sec. used for last three expressions.

P (kg/cm^2)	ε at frequency (~/sec.) 600	1000	2000	d (g/cc.)	$\frac{\varepsilon-1}{\varepsilon+2}\frac{1}{d}$	$\frac{\varepsilon-1}{d}$	$\frac{\varepsilon-1}{d}$
1	2.373	2.373	2.373	0.858	0.3661	1.601	0.6308
150	2.393	2.393	2.393				
500	2.440	2.440	2.440	0.891	0.3643	1.617	0.6311
1,000	2.488	2.490	2.486	.912	.3632	1.628	.6324
2,000	2.575	2.573	2.571	.950	.3619	1.653	.6350
3,000	2.629	2.630	2.627	.975	.3607	1.668	.6371
4,000	2.686	2.684	2.684	1.000	.3593	1.684	.6380
5,000	2.732	2.734	2.729	1.022	.3580	1.693	.6383
6,000	2.775	2.775	2.772	1.042	.3564	1.702	.6384
8,000	2.851	2.851	2.849	1.072	.3557	1.726	.6419
9,500	2.902	2.902	2.900	1.088	.3564	1.747	.6461
% Change			+22.2	+26.8	−2.65	+9.12	+2.43

Table II.

Toluene at $75 \pm \frac{1^\circ}{20}$ C.

$C_g = 53.89 \mu\mu f$. Pressure used: Lowest = 1 kg/cm^2
Highest=11,926 kg/cm.^{2}

P (kg/cm^2)	ε at frequency (~/sec.) 600	1000	2000
1	2.294	2.277	2.275
150	2.341	2.319	2.317
1,000	2.450	2.432	2.430
2,000	2.525	2.513	2.510
3,000	2.609	2.592	2.584
4,000	2.646	2.641	2.635
5,000	2.711	2.696	2.687
6,500	2.762	2.748	2.741
8,000	2.824	2.813	2.802
10,000	2.885	2.874	2.867
12,000	2.947	2.938	2.928
% Change			+28.7

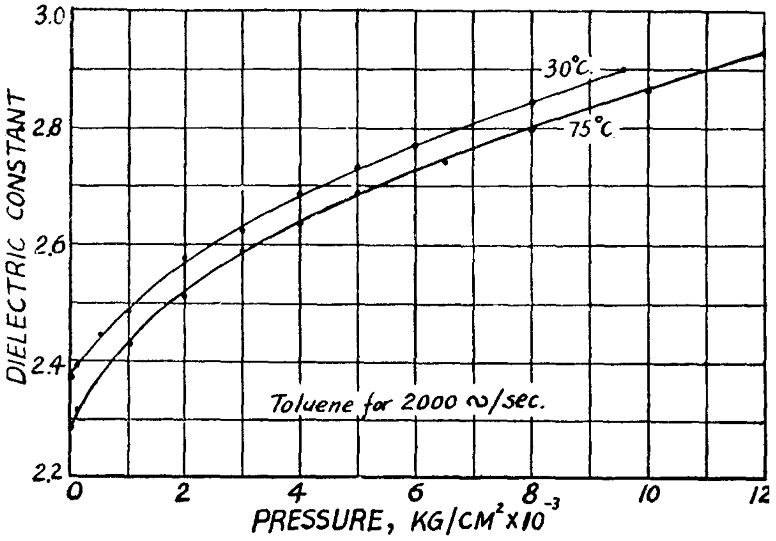

FIG. 8.

From the result of the present work the dielectric constant of toluene is 2.373 (30°.0C, $\lambda=1.5\times10^7$cm.) and 2.275 (75°.0C, $\lambda=1.5\times10^7$ cm.). These values as well as the following are referred to atmospheric pressure. Compare these with 2.37 (14°.4,∞);[22] 2.515 (-83°,∞), 2.33 (16°.5,∞);[23] 2.31 (19°,73 cm);[24] 2.385 (20°,∞);[25] 2.39 (21°,5×10^5cm.)[26], a good check. Here ∞ denotes that the wavelength used was greater than 10^4 cm.

The average temperature and pressure coefficients of the dielectric constant for toluene are listed below.

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(22) H. Landolt and H. John, ZS. ph. Ch. 10, 289 (1892).

(23) R. Abegg, Wied Ann. 60, 54 (1897) and 65, 229 (1898).

(24) P. Drude, ZS. ph. Ch. 23, 267 (1897); Wied. Ann. 64, 131 (1898); Ann. d. Phys., 8, 336 (1902).

(25) K. Tangl, Ann. d. Phys. 10, 748 (1903).

(26) W. H. Hyslop and A. P. Carman, Phys. Rev. 15, 243 (1920).

Table III.

Average Temperature Coefficient, $\bar{\alpha}$, of Toluene at 1 kg/cm^2 and $\lambda > 10^4$cm.

Temperature Range	$\bar{\alpha} \times 10^3$	Observer
4°–45°C.	1.17	Palaz[27]
6°–30°	1.53	Negreano[28]
0°–30°	0.921	Ratz[2]
at 15°	9.077	Tangl[25]
30°–75°	0.937	Writer

Table IV.

Average Pressure Coefficient, $\bar{\beta}$, of Toluene ($\lambda > 10^4$cm.).

Temperature	Pressure Range	$\bar{\beta} \times 10^5$	Observer
19.°18C.	0–500 kg/cm^2	5.30	Ortvay[3]
22.°75	0–60	5.92	Grenacher[6]
30°	1–150	5.63	Writer
30°	1–500	5.58	
75°	1–150	12.3	

(2) Carbon Bisulphide.

Many experimental data have been obtained for his liquid, possibly because it is easy to work with. They will be quoted and compared with those of the present work.

All the measurements were taken with the same filling of the liquid. For the 30°C run, the high pressure press leaked

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(27) A. Palaz. Journ. d. Phys., 5, 570 (1886).
(28) D. Negreano, C. R., 114, 345 (1892).

at about 12,000 kg/cm^2 but did not leak at lower pressures. The capacity measurements took about 8 minutes. During this time interval the pressure was lowered by 90 kg/cm^2. The pressure for every frequency was corrected in a way previously described. As a matter of fact, this is the only occasion that I have to use such corrections.

The values of density at two temperatures and various pressures are due to Prof. Brigman,[29] assuming the density at 0°C and atmospheric pressure to be 1.292. The values at 75°C were obtained by taking the mean of those at 70°C and 80°C, and those at 6500 kg/cm.^{2} were the mean of those at 6000 and 7000 kg/cm.^{2} Since the liquid boils at about 47°C, the lowest pressure used for 75°C run was about 150 kg/cm.^{2}

Table V.

Carbon Bisulphide at $30 \pm \frac{1^\circ}{20}$ C.

$C_g = 53.85 \mu\mu f$. Pressure used: Lowest = 1 kg/cm,^{2}
Highest=11,824 kg/cm.^{2}

ε at 2000∼/sec. used for the last three expressions.

P (kg/cm^2)	ε at frequency (∼/sec.)			d(g/cc.)	$\frac{\varepsilon-1}{\varepsilon+2}\frac{1}{d}$	$\frac{\varepsilon-1}{d}$	$\frac{\varepsilon-1}{d}$
	600	1000	2000				
1	2.624	2.622	2.624	1.247	0.2815	1.302	0.4972
50	2.635	2.637	2.637				
500	2.715	2.715	2.717	1.297	0.2807	1.324	0.4996
1,000	2.784	2.784	2.784	1.336	.2791	1.335	.5008
2,000	2.910	2.914	2.914	1.398	.2786	1.369	.5007
3,000	3.001	3.005	3.005	1.447	.2768	1.385	.5066
4,000	3.103	3.105	3.107	1.487	.2774	1.417	.5131
5,000	3.175	3.177	3.117	1.522	.2763	1.430	.5138
6,500	3.285	3.285	3.287	1.565	.2765	1.462	.5195
8,000	3.374	3.376	3.378	1.603	.2759	1.484	.5228
10,000	3.485	3.489	3.487	1.647	.2752	1.510	.5264
12,000	3.582	3.580	3.580	1.687	.2741	1.529	.5287
% Change			+36.4	+35.3	−2.63	+17.4	+6.33

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(29) P. W. Bridgman, Proc. Amer. Acad., 49, 62 (1913).

Table VI.

Carbon Bisulphide at $75 \pm \frac{1^\circ}{20}$ C.

C_g 53.89 $\mu\mu f$. Pressure used: Lowest = 158 kg/cm,^{2}
Highest=12,011 kg/cm.^{2}

ε at 2000∼/sec. used for the last three expressions.

P(kg/cm^2)	ε at frequoncy (∼/sec.)			d g/cc.)	$\frac{\varepsilon-1}{\varepsilon+2}\frac{1}{d}$	$\frac{\varepsilon-1}{d}$	$\frac{\varepsilon-1}{d}$
	600	1000	2000				
1			2.505*	1.179	0.2834	1.277	0.4945
150	2.537	2.534	2.537				
300	2.573	2.572	2.572				
1.000	2.694	2.690	2.693	1.287	0.2803	1.315	0.4981
3,000	2.935	2.932	2.934	1.410	.2779	1.371	.5057
4,000	3.041	3.040	3.038	1.455	.2780	1.401	.5107
5,000	3.115	3.114	3.114	1.492	.2771	1.417	.5127
6,500	3.224	3.223	3.223	1.536	.2771	1.447	.5176
8,000	3.319	3.318	3.318	1.574	.2768	1.472	.5222
10,000	3.433	3.433	3.433	1.618	.2767	1.503	.5272
12,000	3 536	3.535	3.535	1.660	.2759	1.527	.5301
% Change			+41.1	+40.8	−2.65	+19.6	+7.20

*Extrapolated.

At atmospheric pressure, the dielectric constant for Carbon bisulphide is 2.61(—,∞)^{30}; 2.63(—,∞)^{31}; 2.64(17°,73cm.)^{24}; 2.626(20°, ∞)^{25}; 2.644 (13°,∞)^{5}; and from the present work, is 2.624(30°,1.5×10^{7}cm.).

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(30) J. Hopkinson, Phil. Trans., 172, II, 355 (1881).

(31) A. Francke, Wied. Ann. 50, 163 (1893).

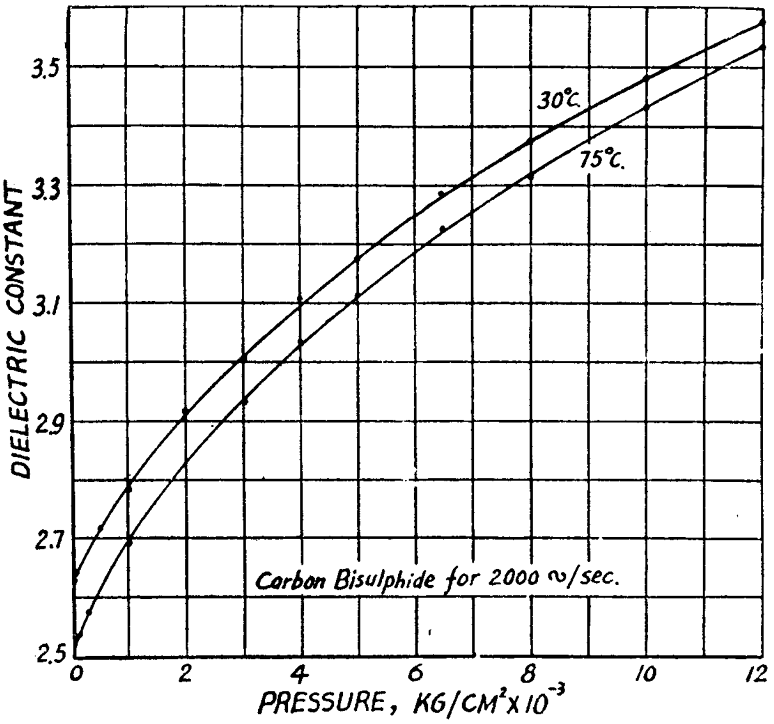

FIG. 9.

Table VII.

Average Temperature Coefficient of ε, $\bar{\alpha}$, of CS_2 at atmospheric pressure and $\lambda > 10^4$cm.

Temperature Range	$\bar{\alpha} \times 10^3$	Observer
3°–17°C.	0.723	Palaz[27]
at 20°	4.000	Cassie[32]
5°–37°	0.966	Ratz[2]
at 20°	0.915	Tangl[25]
30°–75°	1.03	Writer

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(32) W. Cassie, Proc. Roy. Soc., 46, 357 (1889).

Table VIII.

Average Pressure Coefficient of ε, $\overline{\beta}$, of CS_2
($\lambda > 10^4$cm.).

Temperature	Pressure Range	$\overline{\beta} \times 10^5$	λ Observer
13°C.	1–50* kg/cm.^{2}	7.70	Waibel
30°	1–50	10.1	Writer
18.°91	0–500	6.49	Ortvay[3]
20°	1–500	6.85	Kyropoulos[8]
30°	1–500	6.99	Writer
75°	1–300	8.83	Writer
20°	1–3,000	4.70	Kyropoulos[8]
30°	1–3,000	4.52	Writer
75°	150–3,000	5.10	Writer

*The value of ε at 1 and 50 kg/cm.^{2} was calculated from Waibel's equation, good in the range from 1 to 130 kg/cm.^{2} and at 13°C.,

$$\varepsilon = 2.644(1 + 7.47 \times 10^{-5} P - 3.64 \times 10^{-8} P^2).$$

(3) Normal Pentane.

Two fillings of this liquid were used. A run at 30°C was completed with the first filling. It was found that the capacities of the liquid condenser for decreasing pressures were considerably larger than those for increasing pressures. It was suspected that some moisture, possibly in kerosene from the intensifier, might have caused this change, although all the kerosene used for transmitting pressure throughout this research was thoroughly dried by shaking with small metallic potassium wires. In fact, I had great trouble with moisture and have taken all precautions to avoid it. For this reason, petroleum ether was used in both the high pressure cylinders and the intensifier for 30° and also 75° runs. As a rule, we always use kerosene in the intensifier and petroleum ether for 30°C and kerosene for 75°C run in the cylinders. Petroleum ether used for transmitting high pressure has the disadvantage of being more compressible and attacking the rubber washers very much worse than kerosene. However, in the present case I had to use it entirely even for 75°C run. Being a mixture, the boiling point of petroleum ether has a range from 30° to 75°C. Since Normal pentane boils at about 37°C, we could not anyway take readings for the 75°C run below, say, **100** kg/cm.^{2}.

All measurements for 30° and 75° were successfully taken with the second filling.

Table IX.

Normal Pentane.

For 30°C.:— $C_g=53.85$ $\mu\mu f$.
Pressure used: Lowest =1 kg/cm,^{2}
Highest=12,001 kg/cm.^{2}

For 75°C.:— $C_g=53.89$ $\mu\mu f$.
Pressure used: Lowest = 263 kg/cm,^{2}
Highest=12,031 kg/cm.^{2}

P (kg/cm^2)	ε at 30 ± 1/20 °C. for frequency (~/sec.)			ε at 75 ± 1/20 °C. for frequency (~/sec.)		
	600	1000	2000	600	1000	2000
1	1.837	1.833	1.831			1.788*
100	1.852	1.852	1.846			
250				1.830	1.830	1.830
500	1.906	1.906	1.902	1.871	1.869	1.869
1,000	1.959	1.959	1.957	1.926	1.926	1.924
2,000	2.024	2.022	2.022	2.006	2.004	2.002
3,000	2.069	2.069	2.069	2.060	2.056	2.056
4,000	2.114	2.114	2.110	2.112	2.110	2.108
5,000	2.147	2.145	2.145	2.142	2.138	2.138
6,500	2.197	2.197	2.193	2.193	2.189	2.193
8,000	2.232	2.232	2.230	2.232	2.228	2.230
10,000	2.282	2.282	2.280	2.283	2.279	2.281
12,000	2.322	2.320	2.318	2.320	2.320	2.320
% Change			+26.6			+29.7

*Extrapolated.

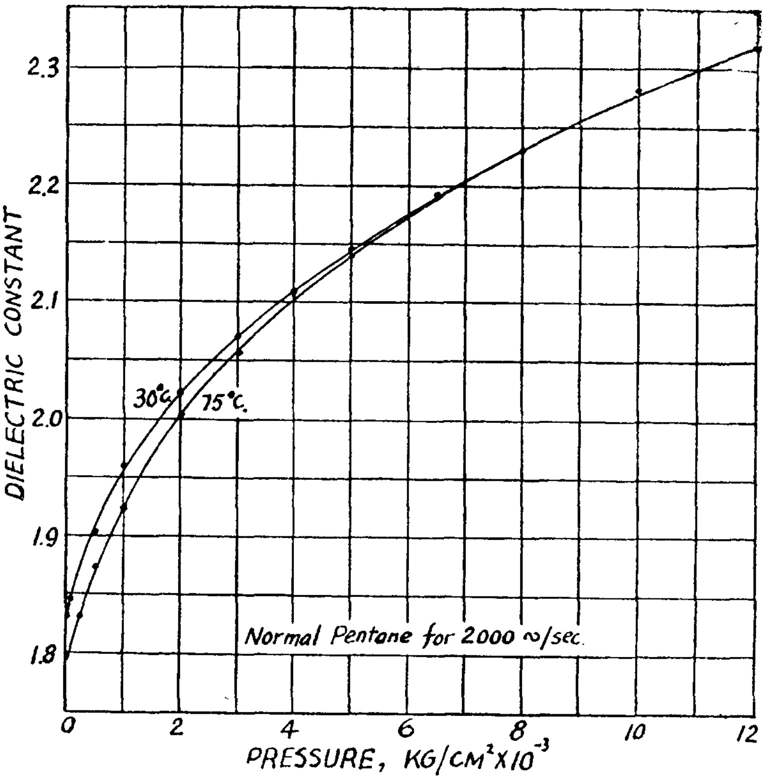

FIG. 10.

The dielectric constant for normal pentane (with 5 carbon atoms) is neither given in any of the tables nor published anywhere that I know of. But the dielectric constants at 17°C and $\lambda=\infty$ are 1.880 and 1.949 for hexane (with 6 carbon atoms) and octane (with 8 carbon atoms) respectively as given in Landolt-Bornstein's physikalisch-chemische Tabellen. Francke[33] gave 1.945 (19°, 6×10^4cm.) for heptane (with 7 carbon atoms). The only value for normal pentane is 1.831 (30°, 1.5×10^7cm.) from the present work.

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(33) C. Francke, Ann. d. Phys., 77, 179 (1925).

The average pressure coefficient of dielectric constant of normal pentane is 7.63×10^{-5} for 1-500 kg/cm.^{2} and 30°C.

(4) Normal Hexane.

The 30°C run was successfully made with the first filling of the liquid. On account of an accident, a second filling was necessary for the 75°C run for which the transmitting liquid was petroleum ether in the high pressure cylinders and kerosene in the intensifier.

The highest pressure used for the 30°C run was about 10,000 kg/cm.^{2} and the lowest pressure for the 75°C run was about 200 kg/cm^2., because the liquid freezes[34] at 30°C at about 10,600 kg/cm.^{2} and boils at atmospheric pressure from 68° to 69°C as given by the manufacturer.

Table X.

Normal Hexane.

For 30°C.:— $C_g = 53.85$ $\mu\mu f$.
Pressure used: Lowest = 1 kg/cm,^{2}
Highest × 10,059 kg/cm.^{2}

For 75°C.:— $C_g = 53.89$ $\mu\mu f$.
Pressure used: Lowest = 198 kg/cm,^{2}
Highest × 12,006 kg/cm.^{2}

P (kg/cm^2)	ε at 30 ± 1/20 °C. for frequency (~/sec.)			ε at 75 ± 1/20 °C. for frequency (~/sec.)		
	600	1000	2000	600	1000	2000
1	1.890	1.888	1.888			1.835*
100	1.905	1.903	1.903			
200				1.865	1.865	1.865
500	1.958	1.956	1.954	1.915	1.915	1.913
1,000	1.995	1.994	1.994	1.961	1.963	1.961
2,000	2.069	2.069	2.069	2.045	2.045	2.041
3,000	2.119	2.119	2.119	2.095	2.093	2.093
4,000	2.158	2.160	2.158	2.134	2.132	2.132
5,000	2.201	2.201	2.201	2.181	2.179	2.177
6,500	2.247	2.245	2.245	2.233	2.229	2.229
8,000	2.294	2.292	2.292	2.279	2.279	2.275
10,000	2.344	2.340	2.340	2.329	2.329	2.325
12,000				2.376	2.376	2.372
% Change			+29.3		–	+29.3

*Extrapolated.

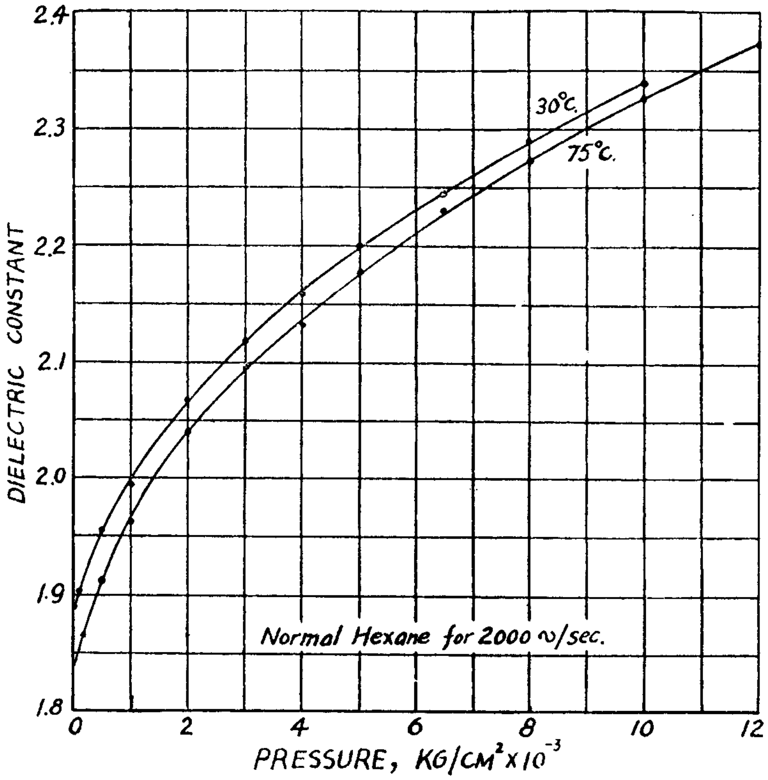

FIG. 11.

The dielectric constant of Normal Hexane at atmospheric pressure was given by several investigator as 1.859 (14°.2,∞)[22], 1.880 (17°,∞)[35], and 1.883 (14°,∞)[5]. From the present work it is 1.888 (30°,1.5×10^{7}cm.) also at atmospheric pressure, and its average temperature coefficient over the range of 30°−75°C. is 6.33×10^{-4}.

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(35) W. Nernst, ZS. ph. Ch., 14, 622 (1894); Wied. Ann., 60, 600 (1897).

Table XI.

Average Pressure Coefficient of ε, β, of Normal Hexane ($\lambda > 10^4$cm.)

Temperature	Pressure Range	$\beta \times 10^5$	Observer
14°	0–100 kg/cm.^{2}	7.95	Waibel[5]
	50–550	6.34	Francke[33]
30°	1–100	8.01	Writer
30°	1–500	6.89	Writer
75°	200–500	8.47	Writer

(5) Ethyl Ether.

Two runs at 30°C and 75°C were made with the same filling of the liquid. As stated before the series resistances used to represent the dielectric losses of the condenser, for decreasing pressures lie on another curve above that for increasing pressures. If we take the corresponding series resistance from the curve for increasing pressures and re-calculate the dielectric constant, the value thus obtained is always smaller and is listed with a parentheses. For the 75°C run petroleum ether was used in both the high pressure cylinders and the intensifier for reasons stated under Normal Pentane. As ether boils at 35°C under atmospheric pressure, the lowest pressure used for the 75°C run was 427 kg/cm.^{2} The value of the density of ether under various pressures were calculated from Prof. Brigman's data, reference 29, p. 56, those for 75°C being the mean value for 70°C and 80°C.

Since ether is very slightly conducting, notably at 75°C, the observed capacity of the ether condenser may be considered to be the sum of the capacities of a perfect dielectric condenser, C_a and an electrolytic one, $C_{a'}$. For the justification of this assumption, see "Iso-amyl Alcohol" below.

Thus $C=C_d+C_e=C_d+f^{-n}X.$

For ether at 75°C, if we plot C against $f^{-.3}$ for various pressures, straight lines are always obtained. The intercepts on the C-axis give the values of C_d. Using these values of capacity, we calculate the dielectric constants which are listed in Table XIII, marked $f=\infty$. It should be noted that the extrapolation is just to eliminate the masked electrolytic capacity and thus to get the real dielectric one which does not represent the value of capacity at infinite frequency, bacause we have not taken account of the absorption bands.

The dielectric loss, represented by series resistance, at 75°C has a maximum value at about 4,000 kg/cm.^{2} for 600 ~/sec., 6,600 kg/cm.^{2} for 1,000 ~/sec., and 7,500 kg/cm.^{2} for 2,000 ~/sec. This seems, at first, to be rather extraordinary. However, it is well known that the loss of a liquid condenser is due to two causes, namely, ionic conduction and molecular friction. The loss due to ionic conduction decreases with increasing pressure. The equation of motion of an oscillating dipole in an impressed sinusoidal e.m.f., $E \sin \omega t$, is

$$\frac{d^2\theta}{dt^2}+k\frac{d\theta}{dt}+c^2\theta=E\sin\omega t$$

where θ is the angular displacement, k and c are constnats and $k\frac{d\theta}{dt}$ is the resisting couple while $c^2\theta$, the restoring couple. The solution of this differential equation is

$$\theta=Ae^{-\frac{1}{2}kt}\cos\left(\sqrt{c^2-\frac{k^2}{4}}\,t+\alpha\right)+\frac{E}{\sqrt{(c^2-\omega^2)^2+k^2\omega^2}}\sin(\omega t-\beta)$$

where A, α and β are constants. In a viscous medium, k is large and the first term soon die out. The dipole thus oscillates with the impressed frequency. The energy comsumed, i.e., the dielectric loss, is proportional to $E^2\left\{(C^2-\omega^2)^2+K^2\omega^2\right\}^{-1}$. The maximum loss occurs when $C=\omega$, i.e., the natural frequency of the dipole is the same as the impressed one, and is inversely proportional to the square of the impressed frequency. When the pressure is increased, the distance between the dipoles is decreased and the restoring couple and thus C is increased. Hence the maximum loss for higher frequency must occur at higher pressure. The sum of this loss and that due to ionic conduction gives the resulting loss as shown in Fig. 13. In the case of iso-amyl alcohol, the ionic loss is so large that the oscillatory dipole loss is negligibly small, thus the resulting loss is constantly decreasing with increasing pressure. In this connection I have the pleasure in discussing it with my friend, Mr. H. P. Soh.

Table XII.

Ethyl Ether at $30 \pm \frac{1^\circ}{20}$ C.

$C_g = 53.85\ \mu\mu f.$ Pressure used: Lowest = 1 kg/cm,^{2}
Highest = 12,065 kg/cm.^{2}

ε at 2000 ~/sec. used for the last three expressions.

P (kg/cm^2)	ε at frequency (~/sec.)			d (g/cc.)	$\frac{\varepsilon-1}{\varepsilon+2}\frac{1}{d}$	$\frac{\varepsilon-1}{d}$	$\frac{\varepsilon-1}{d}$
	600	1000	2000				
1	4.589	4.331	4.190	0.7036	0.7325	4.534	1.488
150	4.808	4.514	4.394				
500	5.150	4.809	4.677	0.7540	0.7303	4.876	1.542
*1,000	5.475	5.121	4.978	.7816	.7294	5.090	1.575
2,000	6.006	5.593	5.435	.8220	.7256	5.395	1.619
*3,000	6.334	5.929	5.774	.8608	.7134	5.546	1.630
4,000	6.899 (6.784)	6.320 (6.279)	6.105	.8875	.7097	5.752	1.658
*5,000	6.922	6.506	6.344	.9101	.7037	5.872	1.669
6,500	7.392 (7.288)	6.886 (6.847)	6.698	.9368	.6993	6.082	1.695
*8,000	7.444	7.114	6.989	.9618	.6927	6.227	1.709
10,000	7.741	7.464	7.359	.9917	.6852	6.413	1.727
*12,000	7.905	4.751	7.686	1.0200	.6767	6.555	1.737
% Change			+83.5	+45.1	−7.6	+44.6	+16.7

*Increasing Pressures.

Table XIII.

Ethyl Ether at $75\pm\frac{1^\circ}{2}$ C.

$C_g=53.89$ $\mu\mu f$. Pressure used: Lowest = 427 kg/cm,^{2}
Highest=12,010 kg/cm.^{2}

ε at 2000 /sec. for the last three expressions.

P (kg/cm^2)	ε at frequency (~/sec.)				d (g/cc.)	$\frac{\varepsilon-1}{\varepsilon+2}\frac{1}{d}$	$\frac{\varepsilon-1}{d}$	$\frac{\varepsilon-1}{d}$
	600	1000	2000	∞				
1			3.700**					
500	4.605	4.244	3.989	3.93	0.7155	0.6975	4.177	1.393
*1,000	5.102	4.522	4.265	4.19	.7491	.6958	4.359	1.422
2,000	6.549	5.294	4.793	4.67	.8029	.6954	4.724	1.481
*3,000	7.472	5.764	5.157	4.99	.8352	.6955	4.977	1.522
4,000	9.110 (9.012)	6.526 (6.432)	5.544 (5.512)	5.30 (5.27)	.8688	.6933 (.6913)	5.231 (5.193)	1.560 (1.552)
*5,000	10.107	6.954	5.824	5.53	.8927	.6907	5.404	1.583
6,500	13.420	8.151 (8.020)	6.373 (6.301)	5.88 (5.85)	.9205	.6972 (.6938)	5.837 (5.759)	1.656 (1.640)
*8,000	13.211	8.392	6.594	6.15	.9465	.6877	5.910	1.657
10,000	16.413 (14.670)	9.243 (9.167)	7.067 (7.017)	6.46 (6.48)	.9763	.6854 (.6835)	6.214 (6.163)	1.698 (1.689)
*12,000	14.559	9.145	7.255	6.77	1.0038	.6733	6.231	1.688
% Change			+96.0		+40.3	−3.5	+49.2	+21.2

*Increasing Pressures.

**Extrapolated.

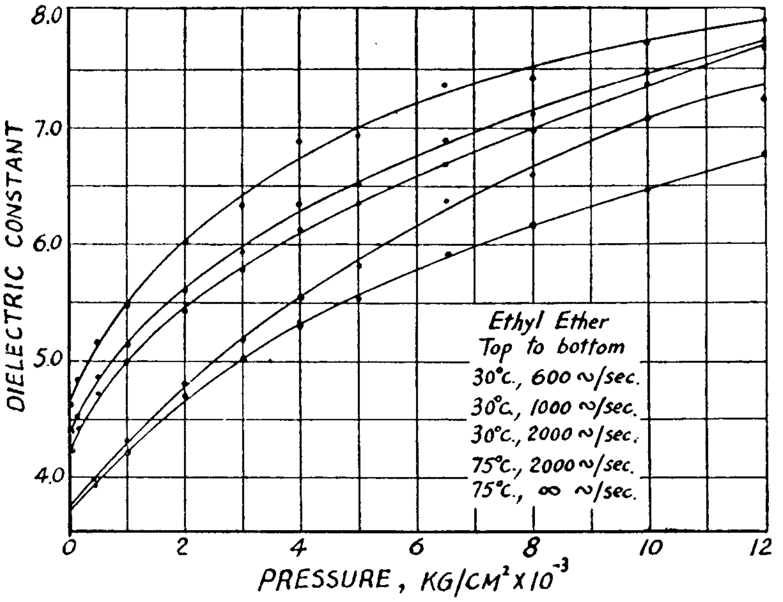

FIG. 12.

Table XIV.

The Dielectric Loss of the Ether Condenser at 75°C. represented by Series Resistance in 10^5 ohms calculated from equation (4).

f (~/sec.) P (kg/cm².)	600	1000	2000
427	3.87	1.41	0.381
* 1,250	4.06	1.54	.405
1,986	4.65	1.83	.501
* 3,145	4.67	1.87	.510
4,010	4.88	2.12	.593
* 5,120	4.70	2.10	.598
6,630	4.39	2.27	.694
* 8,125	4:21	2.12	.637
9,995	4.67	2.08	.647
*12,010	3.69	1.91	.574

*Increasing Pressures.

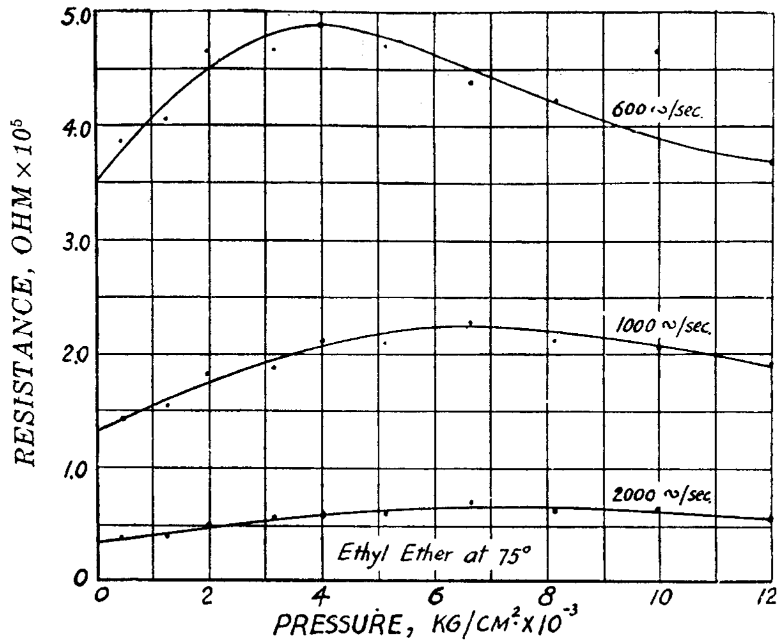

FIG. 13.

From the present investigation, the dielectric constant of ethyl ether at atmospheric pressure and 2000 ~/sec., or $\lambda=1.5\times10^7$cm., is 4.190 at 30°C. and 3.700 (extrapolated) at 75°C. The previous observers gave 4.368 (18°C. and $\lambda=\infty$)[36] and 4.328 (20°C. and $\lambda=3.50\times10^4$cm.)[8] for the same constant.

Table XV.

Average Temperature Coefficient of ε, α, of Ether at 1 atm. and $\lambda>10^4$cm.

Temperature Range	$-\alpha\times10^3$	Observer
0°–30°C.	4.59	Ratz[2]
18°–40°C.	4.30	Tangl[25]
30°–75°C.	2.76	Writer

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(36) B. B. Turner, ZS. ph. Ch., 35, 385 (1900).

Table XVI.

Average Pressure Coefficient of ε, $\bar{\beta}$, of Ether.

Temperature	λ	Pressure Range	$\beta \times 10^4$	Observer
19.°C.	$\lambda > 10^4$cm.	1–250 Kg/cm.^{2}	2.36	Ratz[2]
17.°4	$\lambda > 10^4$	1–500	1.75	Ortvay[3]
21.°3	$\lambda > 10^4$	10–60	2.19	Grenacher[6]
20.°0	3.50×10^4	1–500	2.03	Kyropoulus[8]
20.°0	3.50×10^4	1–3000	1.13	
20.°0	3.50×10^4	500–3000	0.948	
30.°0	1.5×10^7	1–150	3.19	Writer
30.°0	1.5×10^7	1–500	2.21	
30.°0	1.5×10^7	1–3000	1.07	
30.°0	1.5×10^7	500–3000	0.844	
75.°0	1.5×10^7	1–500	1.51	
75.°0	1.5×10^7	1–3000	1.11	
75.°0	1.5×10^7	500–3000	1.03	

(6) Iso-Amyl Alcohol.

This liquid is slightly conducting. Measurements could be taken at temperatures higher than that of the room. Direct substitution parallel resistance method as shown in Fig. 6 was used up to about 8000 kg/cm.^{2} pressure. The dielectric loss of the liquid condenser was found constantly decreasing with pressure up to 12,000 kg/cm.^{2} At 12,000 kg/cm.^{2} the loss was comparatively much smaller than for low pressures and direct substitution series resistance method as shown in Fig. 5 had to be used. At 10,000 kg/cm.^{2}, insufficient high resistance boxes were available and measurements could not be taken, for the parallel or the series resistance was all larger than 2×10^5 Ohms.

The distributed capacity of the parallel high resistance could hardly be determined accurately and is estimated to be about $2\mu\mu f$, while the smallest capacity under measurement is $268\ \mu\mu f.$, thus the error introduced on this account is less than 1%. The final results, therefore, should not be expected to a greater precision than 1%. Thus the small corrections such as the quartz pin condenser and change of the geometrical capacity due to pressures up to 12,000 kg/cm.^{2} and temperature variation not over 3°C are all negligible. The geometrical capacity of the condenser may well be assumed equal to the capacity of the condenser with air at atmospheric pressure as dielectric. Measurements of the capacity of the air condenser at 20.°35C and 76.32 cm. mercury gave $18.6\ \mu\mu f.$ for 600 ~/sec., $18.5\ \mu\mu f.$ for 1000 ~/sec., and $18.5\ \mu\mu f.$ for 2000 ~/sec. The average value of $18.5\ \mu\mu f.$ will be considered as the geometrical capacity of the condenser. The average temperature during the entire run was 22.56°C with a maximum difference of 0.75°C. The correction for the capacity of the liquid condenser for this maximum temperature variation is about 0.2% and therefore negligible. The density of iso-amyl alcohol at 20°C (Ref. 29, p. 53) is used in the calculation since it differs from that at 22.56°C less than ¼% for all values of pressure.

Table XVII.
Iso-Amyl Alcohol at 22.4±0.4°C.
$C_g=18.5\ \mu\mu f,\qquad \Sigma=C/C_g.$

P (kg/cm^2)	t °C.	C ($\mu\mu f$) at frequency (~/sec.)				ε
		600	1000	2000	∞	
1	22.78	388	306	268	258	13.9
282	22.78	385	307	273	263	14.2
448	22.75	373	307	276	267	14.4
1,104	22.72	357	310	289	283	15.3
2,134	22.70	349	318	307	302	16.3
*3,071	22.03	340	326	320	318	17.2
4,170	22.74	347	337	333	332	17.9
*5,022	22.13	345	341	340	339	18.3
6,809	22.75	349	347	347	346	18.7
*7,942	22.30	362	357	354	353	19.1
*12,101	22.45	630	467	387	367	19.8

*Increasing Pressures.

From Table XVII, it will be noticed that the capacity of the liquid condenser for 1000 ~/sec. and 2000 ~/sec. up to about 8000 kg/cm.^{2} increases not so rapid as we should expect. At first sight, it is rather extraordinary that for 600 ~/sec., the capacity is constantly decreasing to a minimum at about 3000 kg/cm.^{2} and then increasing again. However, if we remember that iso-amyl alcohol is slightly conducting, the abnormality can easily be explained. The observed capacity, C, is in reality the sum of the capacities of a dielectric and an electrolytic condenser. The capacity of the dielectric condenser, C_d, increases with increasing pressure and is independent on the frequency within the range used as shown in the cases of toluene, carbon bisulphide, normal pentane, and normal hexane. The capacity of the electrolytic condenser, C_e, decreases with pressure due to the increase of viscosity of the alcohol. It also decreases with increasing frequency and vanishes for infinite frequency. Thus we may write

$$C = C_d\,(p) + C_e\,(p,f)$$

If we plot the observed capacities at different frequencies as ordinates and the inverse square of the frequencies as abscissae, we get invariably a straight line. This suggests, for the present case,

$$C = C_d\,(p) + X\,(p) \cdot \frac{1}{f^2}$$

To get the real dielectric capacity, C_d, all we have to do is to extrapolate the observed capacities to infinite frequency. The masked C_e is thus eliminated, for at high frequency the last term in the above equation is negligible. It should be noted that the value of C_d thus obtained does not represent the capacity of the liquid condenser at infinite frequency because we have not taken account of the absorption bands.

The capacity of the alcohol condenser changes with time, the more so the lower the frequency. Thus

Table XVIII.

Capacity of Iso-Amyl Alcohol Condenser at Atmospheric Pressure

Date (1927)	t°C.	$C(\mu\mu f.)$ at frequency (~/sec.)			
		600	1000	2000	∞
June 9	21.20	393	309	271	259
10	22.78	388	306	268	258
12	21.90	429	323	271	258
14	21.10	414	315	270	257

Note that for 600 ~/sec., the largest difference of capacity is 11% which cannot be attributed to the change of temperature of less than 1°C. and the pressure change of a few cm. of mercury, for the average temperature coefficient between 0° and 30°C. is -7.57×10^{-3} and the average pressure coefficient between 1 and 300 kg/cm^2 is 4.2×10^{-5} as given by Ratz[2] and from the present work, the average pressure coefficient between 1 and 250 kg/cm^2 is 8.58×10^{-5} and between 1 and 500 kg/cm^2 is 8.49×10^{-5}. However, if we extrapolate in a way just described to infinite frequency the capacity is practically constant as shown in the last column. For this reason only the dielectric constant calculated from C_a, the capacity for infinite frequency extrapolated from the observed capacities, will be given in the following table.

Table XIX.

Iso-Amyl Alcohol at 22.4±0.4°C.

$C_g=18.5\ \mu\mu f.$ Pressure used: Lowest = 1 kg/cm,^{2}
Highest=12,101 kg/cm.^{2}

P(kg/cm^2)	ε	d(g/cc.)	$\frac{\varepsilon-1}{\varepsilon+2}\frac{1}{d}$	$\frac{\sqrt{\varepsilon-1}}{d}$	$\frac{\varepsilon-1}{d}$
1	13.9	0.812	0.999	15.9	3.36
250	14.2				
500	14.5	0.843	0.971	16.0	3.33
1,000	15.2	0.867	0.953	16.4	3.34
2,000	16.2	0.903	0.925	16.8	3.36
3,000	17.1	0.930	0.906	17.3	3.37
4,000	17.8	0.952	0.891	17.6	3.38
5,000	18.3	0.971	0.877	17.8	3.38
6,,500	18.6	0.995	0.859	17.7	3.34
8,000	19.1	1.013	0.847	17.9	3.34
12,000	19.8	1.062	0.812	17.7	3.25
Max. % difference	+42.4	+30.8	−18.7	+12.6	4.0

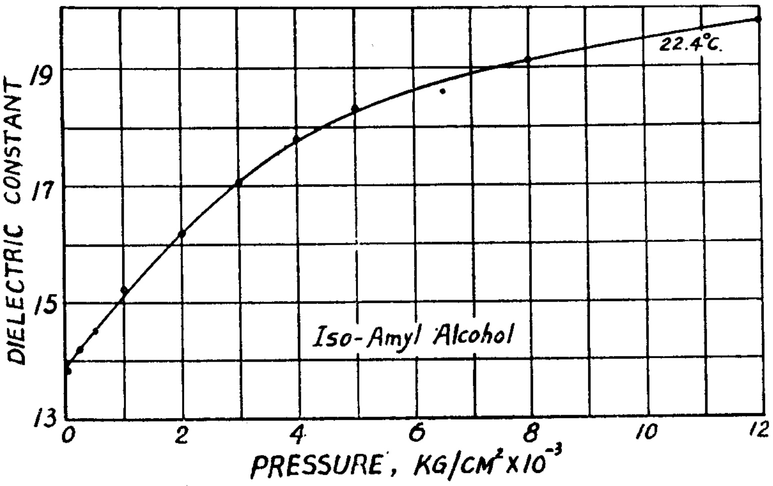

FIG. 14.

IV. General Discussion of the Results.

(A) Accuracy of the Results.

The dielectric constants in the pressure range from 1 to 12000 kg/cm.^{2} given above are accurate to 1/10% for Toluene, Carbon Bisulphide, N-Pentane, N-Hexane at 30° and 75°C, and Ethyl Ether at 30°C, to about 2/10% for Ethyl Ether at 75°C and to 1% for Ethyl Ether at 75°C and to 1% for Iso-Amyl Alcohol at 22.°4C.

(B) Constancy of the Clausius-Mosotti's Expression.

The Clausius-Mosotti's expression, $\frac{\varepsilon-1}{\varepsilon+2}\cdot\frac{1}{d}$, always decreases with increasing pressure for all the six liquids investigated as shown in the tables above and Fig. 15. below. It is interesting to note that from table XX, the decrease is more the greater the electric moment.[37] For Iso-Amyl Alcohol, this expression decreases symptomatically to the pressure axis.

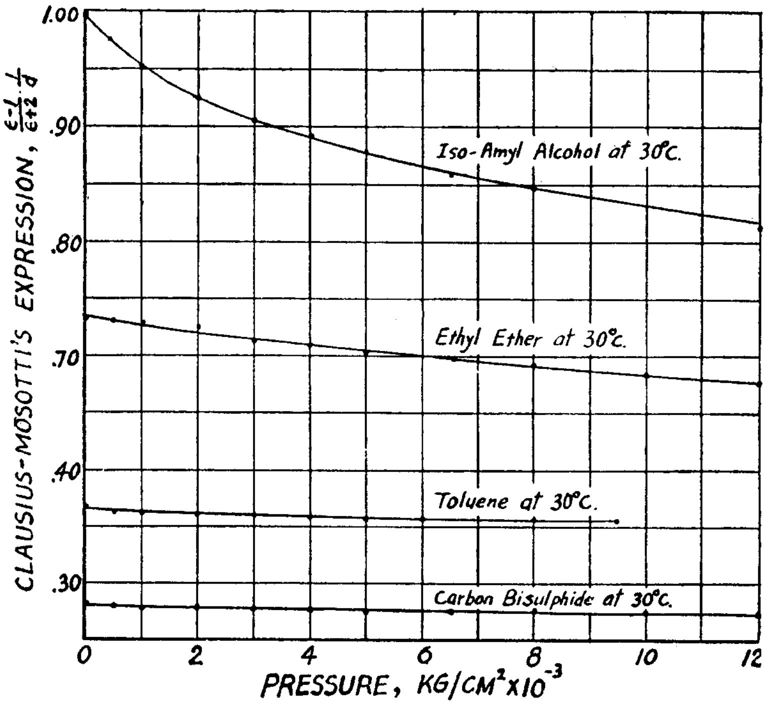

FIG. 15.

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(37) C. P. Smyth, Dielectic constant and Molecular Structure, Appendix I. (Chemical Catalog Co., 1931).

Table XX.

Decrease of Clausius—Mosotti's Expression with increasing Pressure.

Liquids	Pressure Range (kg/cm^2)	% Decrease of $\frac{\varepsilon-1}{\varepsilon+2}\frac{1}{d}$			Electric Moment $\times 10^{18}$
		22.°4C.	30.°0C.	75.°0C.	
CS_2	1—12,000	—	2.6	2.7	0.00
Toluene	1— 9,500	—	2.7	—	0.4
Ether	1—12,000	—	7.6	—	1.12
Ether	500—12,000	—	—	3.5	1.12
Iso-Amyl Alcohol	1—12,000	18.7	—	—	1.7

The decrease of the Clausius-Mosotti's expression with increasing pressure might be due to two causes. In the first place, as the density increases due to increasing pressure, the interaction between the temporary or permanent or both dipoles decreases their orientation in an applied field, thus the polarization and hence the dielectric constant decreases. This decrease of the dielectric constant causes the decrease of the Clausius-Mosotti's expression with increasing pressure. Secondly, due to the increase of molecular association under high pressure the number of particles per unit volume, which has been assumed to be proportional to the density, is decreased. The density used in calculation is thus too large and the Clausius-Mosotti's expression should be expected to decrease with increasing pressure. Molecular association of iso-amyl alcohol will explain the comparatively much larger decrease in the Clausius Mosotti's expression. It is interesting to note that from Table XX, the larger is the electric moment of the liquid, the greater the percentage decrease of the Clausius-Mosotti's expression.

In conclusion, I wish to express my great indebtedness to Professor Bridgman for his constant interest and valuable suggestions during the research carried out in his laboratory, Harvard University, U. S. A. from 1925 to 1927. Thanks are also to Professor Field for his help.