

# The Influence of Pressure on the Dielectric Constant of Carbon Dioxide up to 1000 Atmospheres between 25 $^{\circ}$ and 150 $^{\circ}$ C

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XI. *The Influence of Pressure on the Dielectric Constant of Carbon Dioxide up to 1000 Atmospheres between 25° and 150° C.*

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30th Communication of the Van der Waals Fund.

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*Introduction.*

It was thought to be of interest to find out whether the polarizability of a molecule is affected by changes of density of the substance, and in the case of a polar molecule, whether the moment is changed. It seemed best to start with a gas, as with this the largest changes in density can be obtained.

Previous measurements of the influence of change of density on the dielectric constant of gases have been carried out amongst others by :—

- (1) TANGI\*—Air, hydrogen and nitrogen up to 100 atms. at 20° ;
- (2) OCCHIALINI and BODAREU†—Air up to 350 atms. at room temperature ;
- (3) WAIBEL‡—Air up to 40 atms. at 14° ;
- (4) KEYES and KIRKWOOD§—CO<sub>2</sub> at 0°, 35°, 70° and 100° and NH<sub>3</sub> at 100°, 125°, 150° and 175° up to 200 atms. ;
- (5) BROXON||—Air and nitrogen at 18° up to 170 atms. ;
- (6) The Authors¶—Nitrogen up to 150 atms. at 25°, 75° and 125°.

They all tested the constancy of the Clausius-Mosotti expression. The first three authors found this expression for air to be independent of pressure within the experimental errors. KEYES and KIRKWOOD, however, found in the case of CO<sub>2</sub> and NH<sub>3</sub> a small increase in the Clausius-Mosotti expression with pressure, to an extent of 4 per cent. for a pressure change from 10 to 150 atms.

\* 'Ann. Physik,' vol. 23, p. 559 (1907) ; vol. 26, p. 59 (1908).

† OCCHIALINI. 'Phys. Z.,' vol. 6, p. 669 (1905) ; OCCHIALINI and BODAREU. 'Ann. Physik.,' vol. 42, p. 67 (1913) ; 'Atti Acad. Lincei.,' vol. 22, pp. 480, 482 (1913).

‡ 'Ann. Physik.,' vol. 72, p. 161 (1923).

§ 'Phys. Rev.,' vol. 36, p. 754 (1930) ; vol. 36, p. 1570 (1930).

|| 'Phys. Rev.,' vol. 37, p. 1338 (1931) ; vol. 38, p. 2049 (1931).

¶ 'Phil. Mag.,' vol. 13, p. 1192 (1932).

They consider two possible explanations for this result :--

- (A) A change of polarizability with pressure ;
- (B) The appearance of a correction term in the Clausius-Mosotti formula.

They conclude that perhaps the first of these two explanations can account for the discrepancies in the case of  $\text{CO}_2$  and that the second one may account for the case of  $\text{NH}_3$ .

BROXON found the dielectric constant of nitrogen up to 150 atms., and of air up to 170 atms., to vary linearly with pressure, implying a change in the Clausius-Mosotti expression due to the deviation from Boyle's Law. The experiments of the authors on  $\text{N}_2$  showed, however, the validity of the Clausius-Mosotti equation up to 125 atms.

In the case of liquids appreciable changes in density can only be obtained by using very high pressures. Therefore, of all the published work, only that of DANFORTH,\* working in BRIDGMAN'S laboratory with various organic substances up to 12,000 atms., will be mentioned. He found that the Clausius-Mosotti expression  $P$  was not independent of pressure, but that  $1/P$  varied approximately linearly with pressure.

In the present case it was decided to work with  $\text{CO}_2$ . This gas could easily be prepared pure and does not attack the material of the condenser. With this gas, it is possible to work through the critical region which has the additional interest that large density changes can be easily obtained.

During the preparation of the work, the paper by IBBS and WAKEMAN† appeared, in which it was claimed that a discontinuity appears in the molecular field at about  $145^\circ$ . They suggest that this might be ascribed to a bending of the molecule, in which case the molecule would become polar. Some extra measurements were therefore carried out in the neighbourhood of this temperature, although, as will be discussed later, at present there are not sufficient isotherms known to enable this question to be settled in the present pressure range.

#### *The Method.*

In principle the method chosen is the ordinary heterodyne one, in which the substance to be investigated is put between the plates of a fixed condenser of known zero capacity. As the capacity is proportional to the dielectric constant of the substance between the plates, determination of the new capacity gives the dielectric constant. In order to determine the change of capacity, the condenser and a parallel variable one are coupled with a coil; condenser and coil forming the vibrating system of a high frequency oscillator, the frequency being  $\nu = \frac{1}{2\pi\sqrt{LC}}$ . When the capacity of the high pressure condenser is increased as a result of an increase of the dielectric constant of the substance between the plates, it is possible to get the original frequency back by diminishing the

\* 'Phys. Rev.,' vol. 38, p. 1224 (1931).

† 'Proc. Roy. Soc.,' A, vol. 134, p. 613 (1932).

capacity of the variable condenser by the same amount. In order to control the constancy of this frequency, the circuit is tuned against another oscillator of a constant wavelength. The heterodyne beat of the two oscillators is such that it gives an audible note. In the system used the standard frequency was 508 kilocycles and was stabilized with piezo-quartz. The beat note was controlled against a tuning fork of 435 cycles to which value the beat note was always adjusted. During the experiments it was found possible to keep the beat constant within one vibration a second for longer than  $\frac{1}{4}$ -hour.

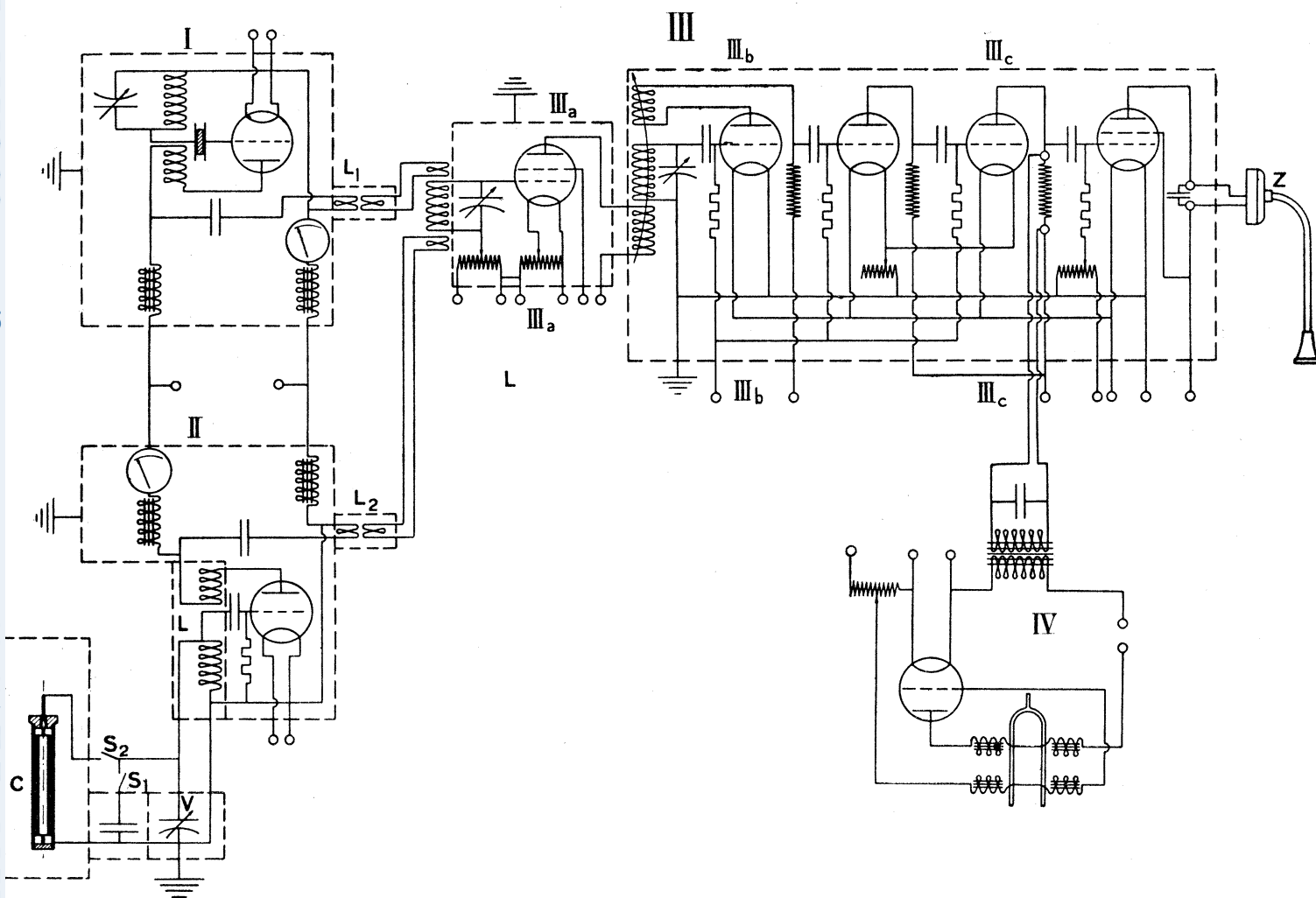


FIG. 1.

*Description of the Apparatus.*

(a) *The electrical circuit.*—A wiring diagram of the circuit used is given in fig. 1. In the diagram, system I shows the standardized frequency of  $\nu = 508$  kilocycles; system II the measuring circuit. Both were coupled with  $L_1$  and  $L_2$  to the amplification

and detector-system, III. System IV shows the tuning fork with the arrangements for keeping it in vibration with a triode valve, the note being coupled to the last stage of the amplifier. The output of the amplifier passed through the loudspeaker (Z). Each of the systems and the coupling coils were separately screened, as shown in the drawing.

As the constancy of a piezo-quartz stabilizer depends on the temperature, the stabilizer of System I was placed in a Dewar vessel. System I, as well as System II, were grid-tuned in order to minimize the influence on the frequency of the mutual inductions of the coils  $L_1$  and  $L_2$  in the anode circuits.

The measuring Circuit II contained the high pressure condenser (C) and the variable condenser (V). Arrangements were made that in any of the measurements the high pressure condenser could be replaced by a set of condensers of known capacity with the switches  $S_1$  and  $S_2$ . This eliminates any change in the leads and the rest of the circuit. The condensers used were from Spindler & Hoyer. The scale of the variable condenser was calibrated by making comparisons from point to point with a small constant condenser. The latter was taken as the standard unit of capacity and all other capacities were expressed in the same unit to avoid the necessity of absolute measurements. The high pressure condenser will be described with the high pressure apparatus. As Circuit II could not be stabilized, much greater care was taken to avoid disturbance by induction or mechanical vibration. Therefore, the coil L was wound on a porcelain cylinder, 6 inches in diameter, with wire 2 mm. thick, kept in position with Glyptal varnish. The coil was placed asymmetrically in a shielded box,  $45 \times 70 \times 45$  cm. In order to avoid Foucault currents, the shielding material was arranged with strips of tinfoil connected together only at one side.

Care was given in the construction of the switches  $S_1$  and  $S_2$  in order to avoid changes in the frequency on opening and reclosing the switch.

Fig. 2 (a) shows a scale-drawing of a switch in the opened position. It will be seen that the movable metal part (A) is then inside a fixed metal tube (B). When open, therefore, this movable part has no capacity in relation to the rest of the switch. Fig. 2 (b) shows the switch closed and it can be seen that the total increase of capacity is given by the length of the rod (A) between the ends of the tubes B and C, irrespective of whether the moving part has come back into exactly the same position or not. During the experiments, it was found that these switches gave a reproducibility of at least one beat a second.

The amplification and detector-system III contained a one-stage high frequency amplification IIIa, a detector IIIb, and a three-stage low frequency resistance amplification IIIc.

In order to minimize the influence on the oscillators, the coupling was made as weak as possible, the primary and the secondary of  $L_1$  and  $L_2$  consisting each of only one winding 2 cm. in cross section and about 2 cm. apart.

The whole electrical circuit was built in a double-walled wooden room about 2 m. by  $2\frac{1}{2}$  m. and 2.80 m. high. The inside was shielded with aluminium plates 0.8 mm.

thick. To avoid induction effects no metal leads from the apparatus were brought out of, and no leads from the mains were brought into, the room.

Arrangements were made to work all switches and the variable condenser from outside and to read the variable condenser and thermometers with telescopes. The loudspeaker was placed inside the room, the horn being removed and replaced by a rubber tube leading outside. Light was admitted through a window shielded with copper gauze.

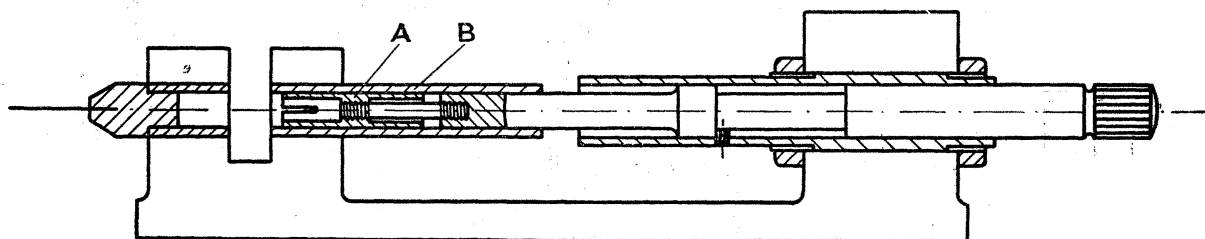


FIG. 2 (a).

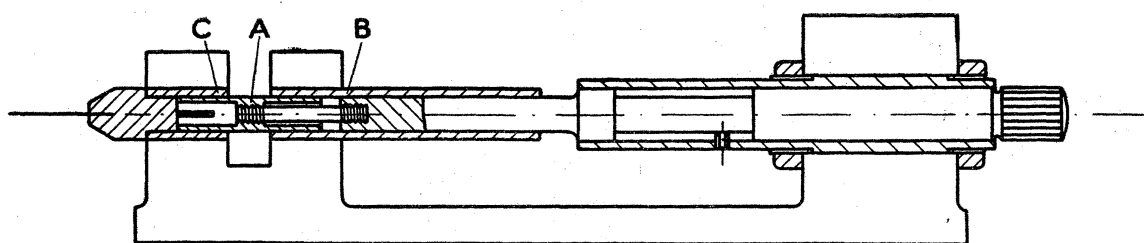


FIG. 2 (b).

The temperature was kept constant within a tenth of a degree in order to minimize variations due to temperature changes in the capacities, battery potentials, etc.

(b) *The high-pressure system.*—A diagrammatic drawing is given in fig. 3: it consisted in principle of four parts:—

- I.—the high-pressure condenser ;
- II.—a mercury gas-compressor with which the gas, supplied from a storage cylinder, was compressed into the condenser ;
- III.—a hydraulic press filled with oil and coupled to the gas-compressor ;
- IV.—the pressure balance for measuring the hydraulic pressure of the oil.

I. *The high-pressure condenser.*—A scale-drawing of the high pressure condenser is given in fig. 4. The electrical part shown in 4 (a) consisted in principle of two coaxial brass cylinders A and B, insulated from each other by two silica discs C and D. In order to decrease the dead space of the apparatus, and at the same time to make provision for adjusting the inner tube inside the outer, a brass rod E was placed inside the inner tube. Between the rod and tube a small gap was left, with grooves opening to both ends, in order to ensure a hydrostatic compression of the cylindrical tube. Conical holes F and G were cut in each end of the rod. With the screw H the rod E was pulled against the steel cone J. At the lower end the rod was kept in position by the steel

ball K pushed by the spring L and screw M. This arrangement ensured an almost frictionless motion in the event of both parts of the apparatus not expanding equally on rapid temperature changes.

The condenser fitted in the steel cylinder N, which was closed by the lens-ring O and nut P. The lead through the steel wall was insulated with the help of the two silica

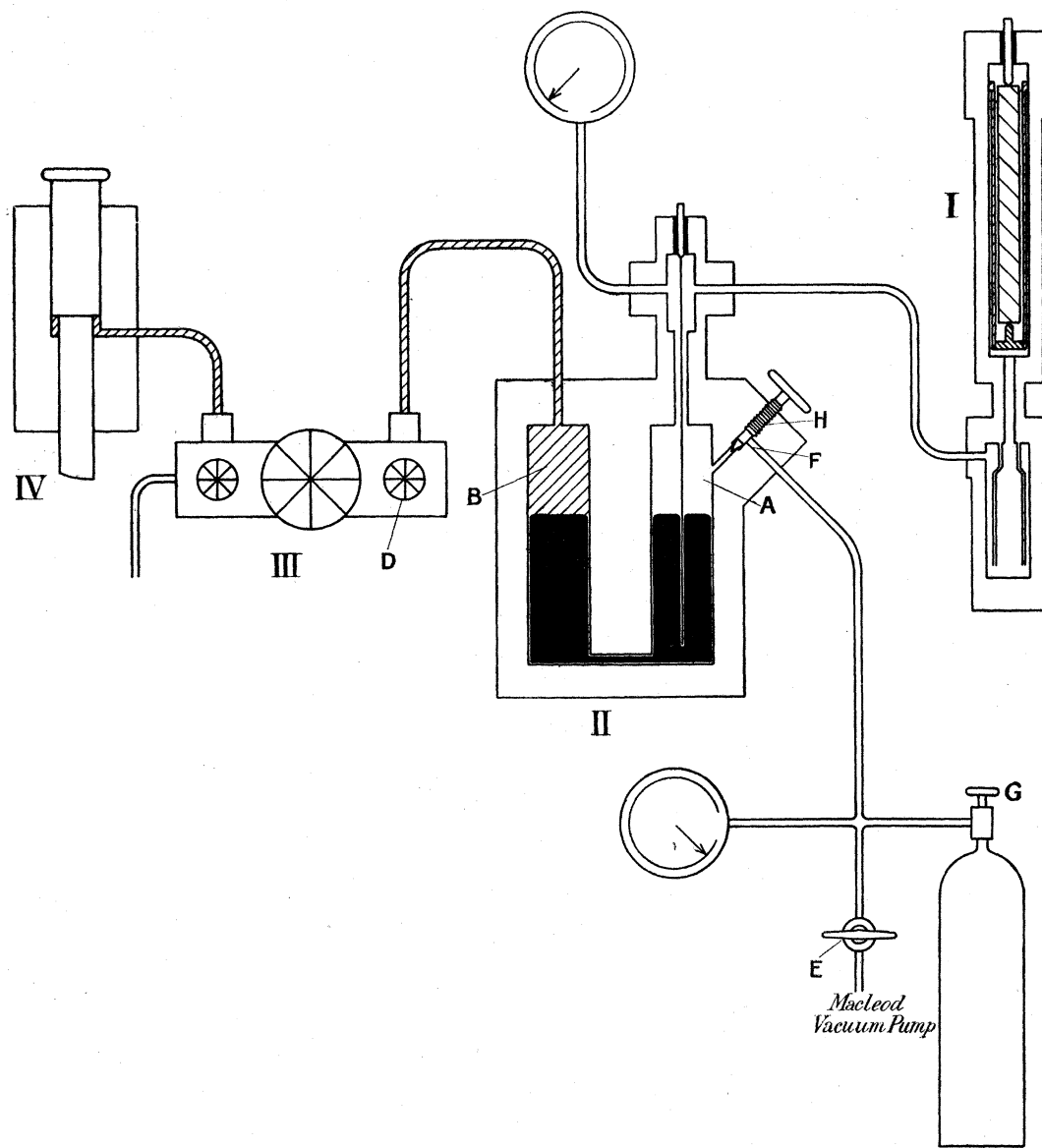


FIG. 3.

discs Q and S. The upper side of the steel plug R and the lower part of the lens-ring O were ground optically flat, as also were the two sides of the silica disc S. For the initial closing before mounting, the parts O, R and S were stuck together with a thin layer of Canada-balsam but as soon as pressure is applied, this in itself keeps the system closed. The steel cylinder N was screwed into the lower part T in which gas was

admitted through the tube U. This lower vessel acted as a receiver should mercury come over from the gas compressor.

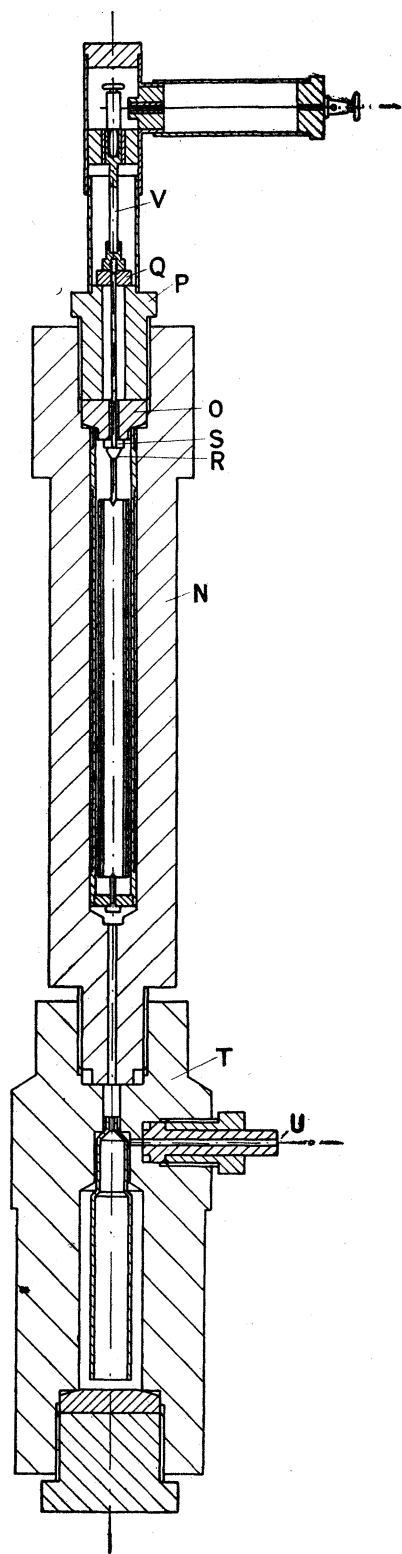


FIG. 4.

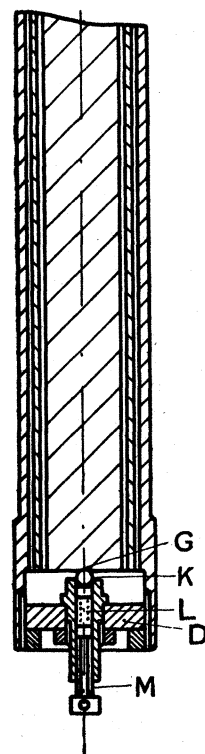
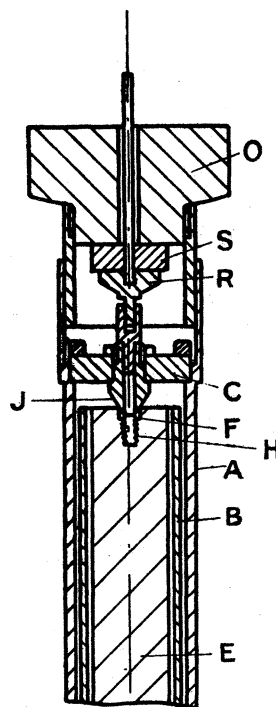


FIG. 4(a).



The connection from the lead V to the high frequency set was shielded from induction effects by a brass tube about 5 cm. in diameter.

II. *The gas compressor.*—Fig. 5 gives a drawing of the compressor. As can be seen, the two holes A and B are connected through C, and were half filled with mercury. D leads to the oil-press, E to the high pressure condenser, F to the storage cylinder filled with  $\text{CO}_2$  under its own vapour pressure, and G is a tube with an inner bore of about 0.1 mm. leading to a spring manometer. (This spring manometer was only used as an indicator.) The pressure condenser was filled by letting  $\text{CO}_2$  in through F and the gas compressed by applying pressure through D.

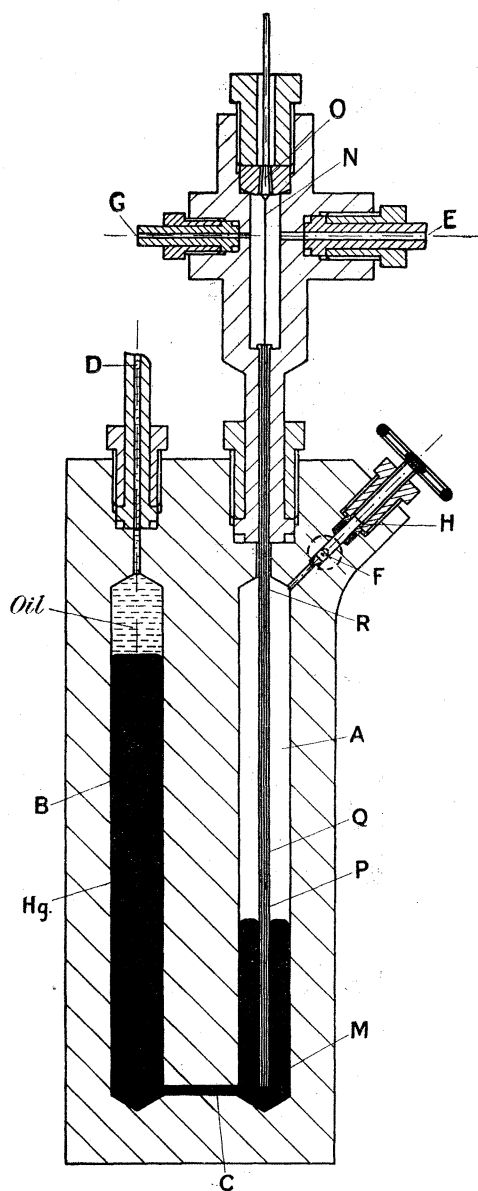


FIG. 5.

As the pressure was measured by the pressure balance coupled to the oil-press, it was necessary to allow for the pressure difference caused by the position of the mercury in A and B, in order to know the pressure in the condenser.

This was calculated from a measurement of the position of the mercury in A by means of the resistance of a platinum wire MN, arranged in A, as shown in the figure. A steel cone O was insulated from the rest of the apparatus by means of a porcelain cone. One end of the platinum wire was attached to O and the other end to the bottom of a steel tube P. A glass tube Q insulated the platinum wire from the steel tube. In order to attain an equal height of mercury inside and outside P, holes were bored at R.

III and IV. *Press and pressure balance.*—The pressure balance used was the usual differential piston type.\* The press was a combined hydraulic and Cailletet-screw press built for 3,000 atms.

#### *Thermostatic Devices.*

Both the thermostat and the room were electrically heated and regulated, the energy being supplied directly from the 220 volt A.C. mains.

In each case, for better regulation, two heating elements were used, one having a maximum output about ten times that of the other. The first was adjusted by hand

\* A. MICHELS. *Ann. Physik.*, vol. 72, p. 285 (1923); vol. 73, p. 579 (1924).

so that the energy given was slightly under that required; the second supplied the additional energy controlled by the automatic regulator. Both regulators were of the contact type, closing as soon as the temperature required was reached. Contact opens and shuts a relay with the help of a wireless valve. The system is that given by D. J. BEAVER and I. J. BEAVER,\* modified to work with alternating current.

The points A and B are connected to the mains. C is the large heating-element adjusted with the rheostat D; E is the additional element and F a second rheostat. The contact thermo-regulator is placed between the points G and H.

When using alternating current the circuit works as follows. When the regulator is open the potential of the grid J cannot follow the alternating potential of point K

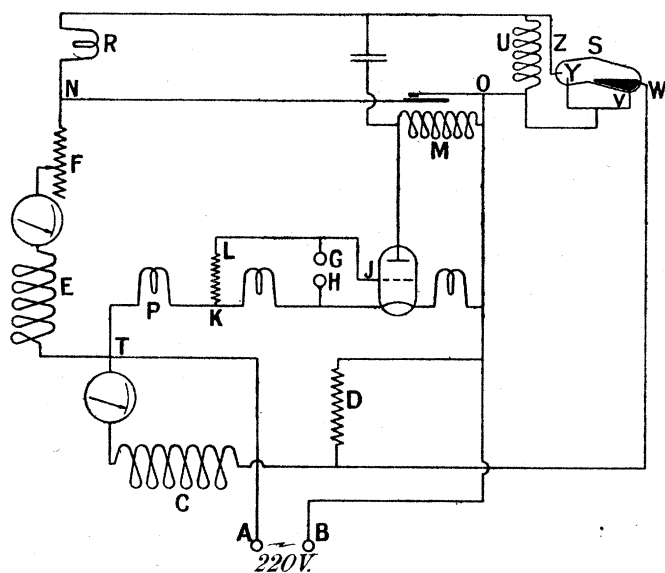


FIG. 6.

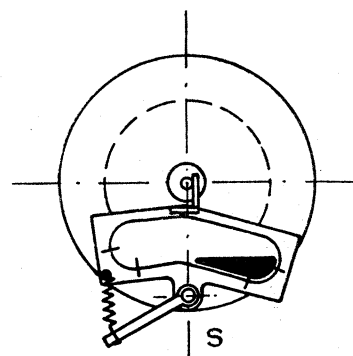


FIG. 6(a).

as the grid leak L is too high. The potential of the grid remains therefore negative and no anode current flows through the primary of the relay M. This stays shut and the additional heating current can pass directly from A through E, F, N and O, back to B. As soon as contact is made, the relay is opened by the anode current of the valve and the heating current passes through the resistance R and is therefore decreased. It was found that using the original circuit of BEAVER and BEAVER, the filament of the valve was destroyed, as occasionally, for a short time after the contacts of the thermo-regulator had opened, the potential of the grid was too high. In order to avoid this, a third resistance P was placed in the filament circuit.

A second alteration was made for the initial heating of the system. A mercury interruptor S was placed in the system, as shown in the drawing. In this position, the current of the main heating element can pass from A through T, C, W, V, O, to B, thus avoiding the resistance D, so that the maximum energy is delivered. As soon as the

\**J. Ind. Eng. Chem.*, vol. 15, p. 359 (1923).

regulator makes contact for the first time, the current of the additional heating-element passing through R passes also through the electro-magnet U; this pulls the mercury interruptor over, breaking the contact between W and V and the current of the main heating-element passes through the resistance D. At the same time, the mercury makes contact between the platinum points Z and Y, short-circuiting U. The interruptor S is so arranged that, when it is once pulled over, it stays in that position. Fig. 6 (a) shows a drawing of the interruptor with electro-magnet.

For the regulation of the room temperature, it was necessary to use a regulator of high heat-absorption and small heat-capacity. Fig. 7 is a drawing of the apparatus.

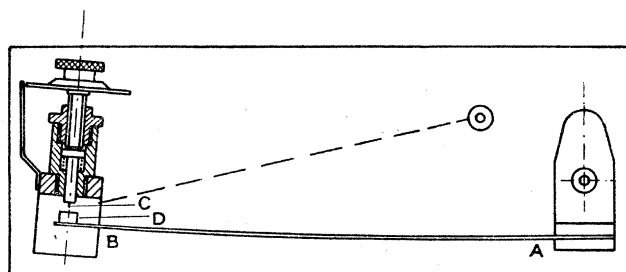


FIG. 7.

A-B is a bi-metallic strip about 0.5 mm. thick, 10 mm. wide and 150 mm. long. Increase of temperature bends this strip to make contact between the platinum point C and the stainless-steel nut D. In order to increase the speed of the regulator, it is possible to coat the bi-metallic strip with carbon-black.

The regulator used in the bath was in principle a contact thermometer. A scale-drawing is given in fig. 8. The bulb A, containing mercury, has a volume of about 60 cc. while the capillary BC has a diameter of about 0.5 mm. Through this capillary at D, is fixed a platinum wire of about 0.02 mm. diameter. When the mercury reaches this wire, it makes contact between D and a second platinum wire, sealed through at E. The regulator can be adjusted by bringing mercury out of, or into, the reservoir F. In order to make it possible to use this regulator up to higher temperatures, the inner tubes F and G are filled with nitrogen and the outer tube H is made so long that the top of G is always under the level of the bath, thus avoiding distillation of mercury to colder parts. An advantage over regulators filled with toluene is not only the higher temperature range, but also the smaller reaction time, as a result of the better thermal conductivity of the mercury. The regulators being connected in the grid circuit of the triode valve, there is no sparking which helps to keep the contacts clean.

#### *Heating Arrangements.*

A scale-drawing of the heating- and stirring-system of the thermostat is given in fig. 9. The heating-elements were so called Backer-elements, consisting of nichrome spirals insulated with magnesium-oxide inside a copper tube. The elements are 5 feet

long. As shown in the drawing, the heating-elements were twisted and fixed through the bottom of the thermostat. The advantage of using copper tubes was that they could be earthed, thus screening any induction effect outside the heating-elements. The stirrer was fitted over the heating-elements and hung in a ball race. The thermostat was filled with spindle oil giving a temperature range up to  $180^{\circ}\text{C}$ . The heating-elements of the room were commercial Arora low-temperature heaters, also screened and earthed at the outside. The fan of a ventilator, driven by a motor outside the room, blew air along the heating-elements and at the same time kept the air of the room in circulation. The room-temperature was generally kept at  $22^{\circ}\text{C}$ . In hot weather, water was circulated through a copper tube round the roof of the room. This made it possible to keep the temperature 5 or 6 degrees below the temperature outside.

The temperature of the bath was read with mercury thermometers divided in hundredths of a degree, one degree corresponding with about 5 cm. scale-length. These thermometers were compared with two sets of thermometers calibrated in the Physikalisch-Technische Reichsanstalt in Berlin. To avoid stem corrections, a periscope\* was used, fig. 10, so that the thermometer could be read totally immersed in the thermostat. The thermometer is held in a brass tube, the bulb fitting closely in a copper block to ensure good thermal contact. This brass tube fits in a second brass tube AA, and can be adjusted so that the scale of the thermometer is in the right position for reading. The scale is illuminated by a lamp B and read by means of the two reflecting prisms C and D and the telescope E.

#### *Purification of the $\text{CO}_2$ .*

The  $\text{CO}_2$  used was purified by three low-temperature distillations of commercial gas. The system used is shown in fig. 11. A is the storage cylinder of commercial  $\text{CO}_2$ , B leads to a three-stage mercury diffusion pump with McLeod vacuum gauge. The whole system was first evacuated, then tap C was closed, liquid air poured into E and solid  $\text{CO}_2$  and alcohol into F. The valve G of the storage cylinder was opened and a slow current of  $\text{CO}_2$  streamed into the apparatus through the  $\text{P}_2\text{O}_5$  tube N, passing F, where it was pre-cooled and the last traces of moisture removed. The pre-cooled gas then condensed against the tube E. Meanwhile, the diffusion-pump was kept working in order to remove any permanent gases. The solid  $\text{CO}_2$  accumulated as a thick rod and when enough had been collected, G and H were closed, tap C opened and the  $\text{CO}_2$

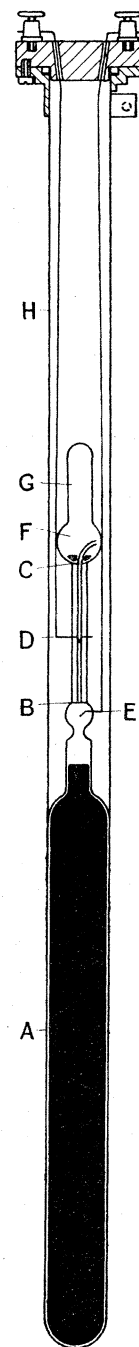


FIG. 8.

\* Cf. MICHELS and GIBSON. 'Proc. Roy. Soc., A,' vol. 134, p. 288 (1931).

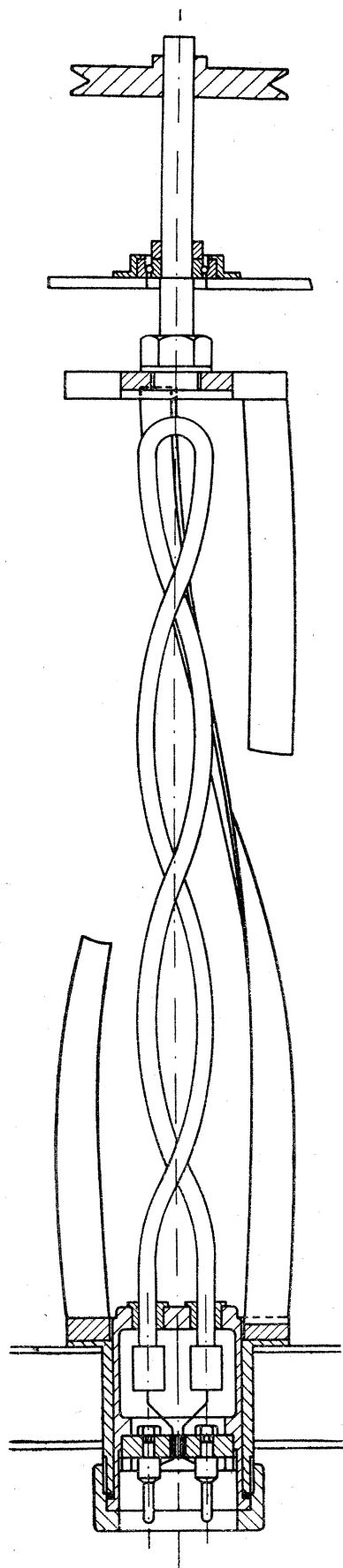


FIG. 9.

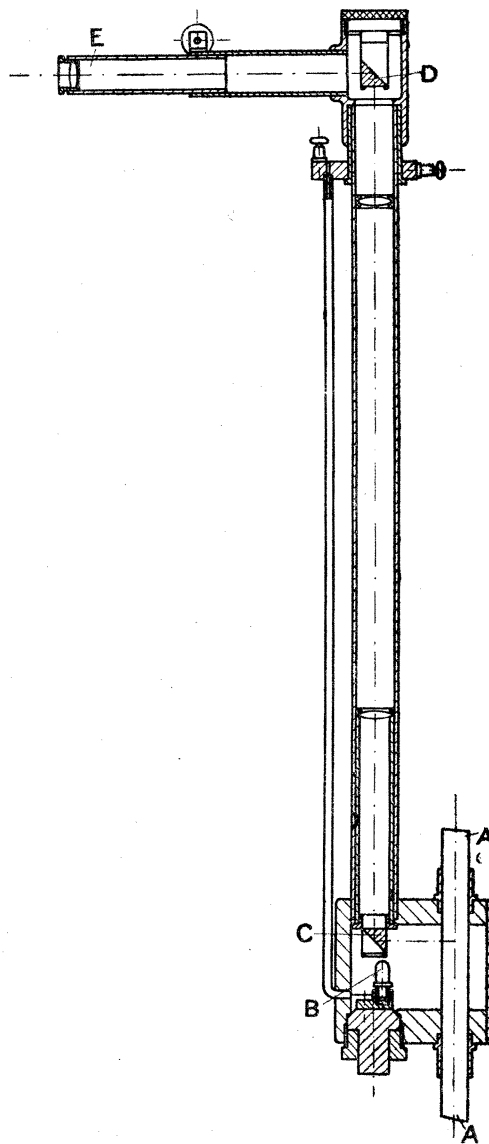


FIG. 10.

distilled in the second cooling-vessel J, allowing the first and the last fraction to escape. After the second distillation was finished, the  $\text{CO}_2$  was distilled—again discarding the first and the last fraction—into the glass vessel K. This glass vessel could stand about 10 atmospheres and was soldered to the copper tube L. When there was enough  $\text{CO}_2$  in this vessel, the steel tap M was closed and the temperature raised until the  $\text{CO}_2$  became liquid and distilled into a special storage cylinder of non-corrosive material, placed in a mixture of solid  $\text{CO}_2$  and alcohol. The distillation took place at a pressure of a few atmospheres.

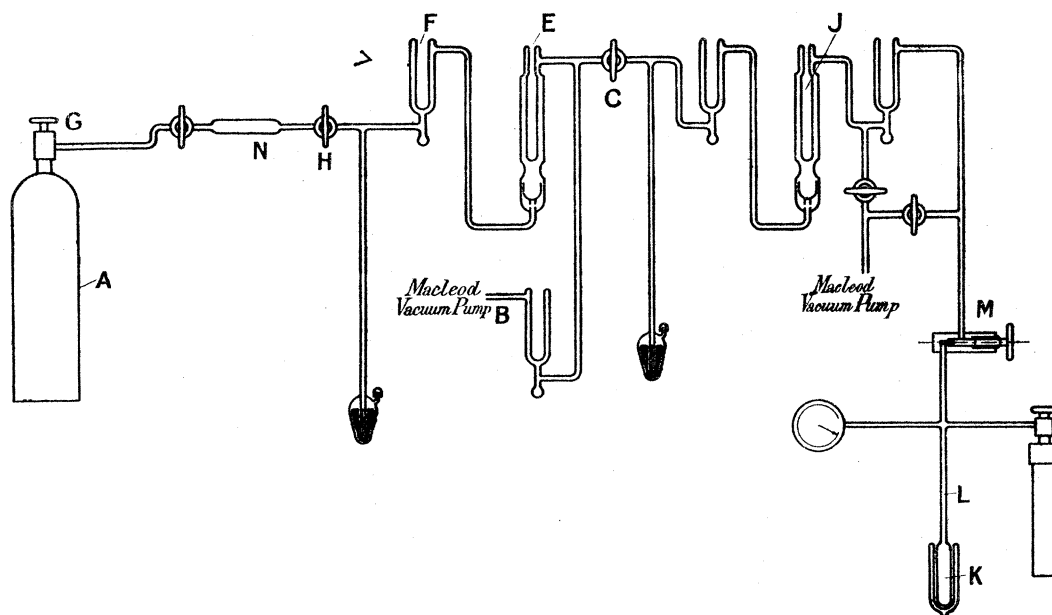


FIG. 11.

*The Calibration of the Apparatus.*

It was first necessary to calibrate the resistance of the platinum wire in the gas compressor in terms of the position of the mercury. This was done by opening A and B, fig. 5, to the air, pouring different amounts of mercury into A and measuring the heights and corresponding resistances. After this, mercury was taken out of the compressor, leaving a known amount correct for working the apparatus.

As the total capacity in the high frequency circuit, fig. 1, System II, includes the capacity of the leads, a special determination of the zero capacity of the high pressure condenser was necessary.

This was done by measuring the difference in capacity of the condenser when evacuated and when filled with benzene.

If the capacity of the condenser evacuated is  $C_0$  and of the leads  $C_l$ , then the total capacity measured in the evacuated state is:—

$$C_1 = C_0 + C_l.$$

When filled with benzene of dielectric constant  $\epsilon$  :

$$C_2 = \epsilon C_0 + C_i.$$

Therefore the measured difference :

$$\Delta C = C_2 - C_1 = (\epsilon - 1) C_0.$$

The benzene used was the purest obtainable from Kahlbaum and was still further purified by twice crystallizing and distilling over sodium. The final melting point was  $5.54^\circ \text{C}$ . The benzene was distilled into a glass bulb and frozen under reduced pressure to remove permanent gases, and the glass bulb sealed.

The condenser was placed in the thermostat in the position in which it was to be used for final measurements and the glass apparatus shown in fig. 12 attached to the steel tube B normally leading to the gas compressor.

The benzene in the sealed bulb A was separated by a glass diaphragm from the rest of the apparatus.

The thermostat was filled and regulated at  $25^\circ$  and the system evacuated through C. This evacuation was continued for several days to remove the large amount of gas that was absorbed on the walls of the metal apparatus. When the vacuum had remained constant for some hours, the capacity  $C_1$  was measured. With the help of a magnet the steel ball D was then dropped on the glass diaphragm to break it. By gently warming A and cooling at E the benzene distilled into the high pressure condenser. Distillation was continued till the benzene level was visible in F. Pressure was then applied from a nitrogen cylinder through the tap G and adjusted to 1 atm. with the help of the open manometer H. The capacity  $C_2$  was then measured. To be certain that there was no gas left in the condenser, some extra pressure was given with the nitrogen and the capacity again measured. The presence of gas or vapour would cause an abnormal change in the capacity.

Benzene was then removed by distilling back into A, cooling it with solid  $\text{CO}_2$  and alcohol, and the capacity  $C_1$  remeasured.

The result found for the zero-capacity was :

$$C_0 = 142.9 \text{ cm.}$$

The value taken for the dielectric constant of benzene was  $2.272$  at  $25^\circ \text{C}$ ., given by HARTSHORN and OLIVER.\*

#### *The Filling of the High Pressure Condenser.*

The condenser was then coupled to the compressor, fig. 3, and the valve D shut. Condenser and compressor were evacuated through F and E and filled with  $\text{CO}_2$  by

\* HARTSHORN and OLIVER. 'Proc. Roy. Soc.,' A, vol. 123, p. 664 (1929).

opening valve G. As the measurements were to be started with pressures less than the saturated vapour pressure in the storage cylinder, the mercury was forced to the top

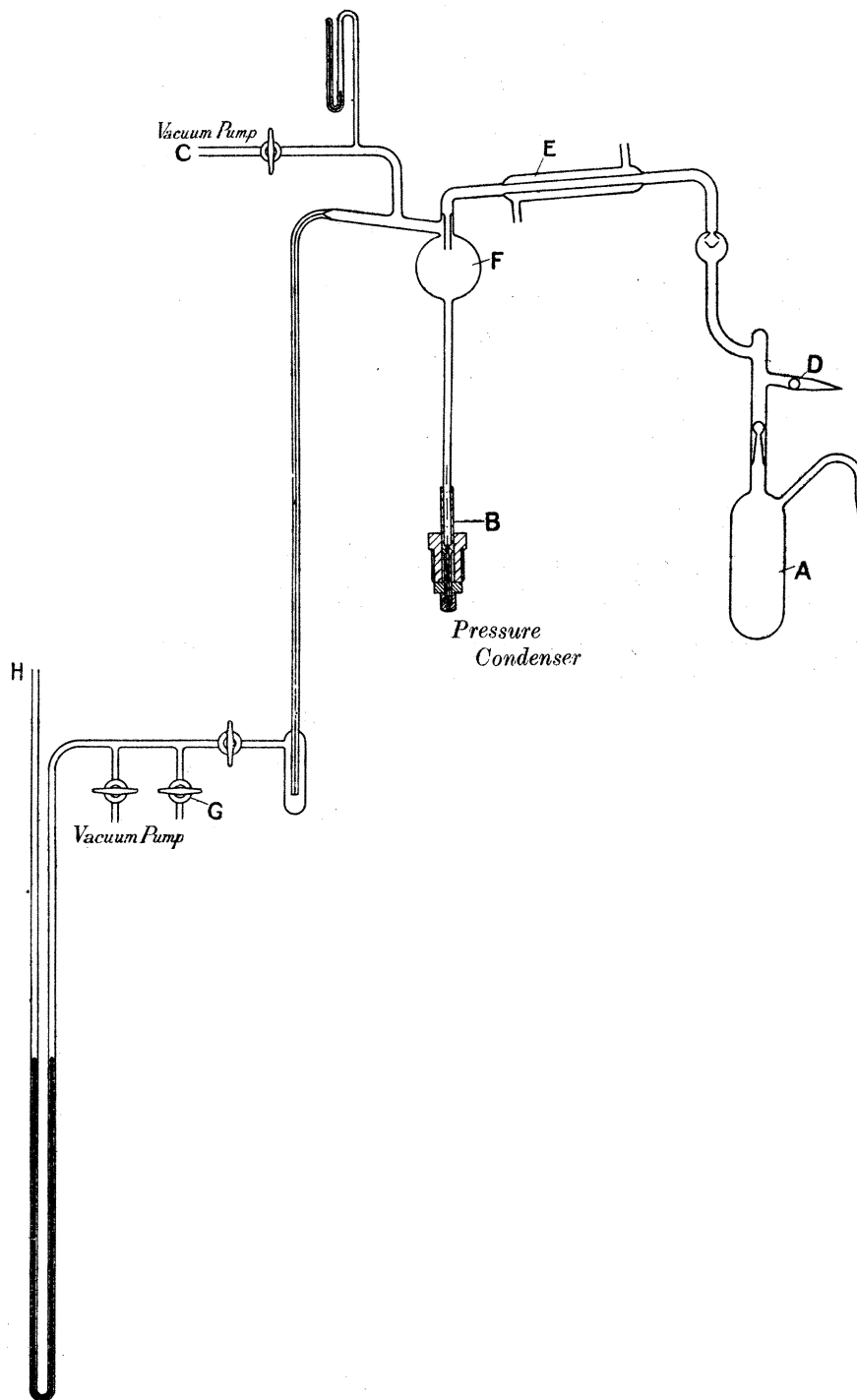


FIG. 12.

of tube A with the hand press. Part of the  $\text{CO}_2$  was thus returned to the storage cylinder and just before the mercury level reached the valve F, this was shut. On



lowering the pressure in the press the mercury level in A sank, the gas could expand and measurements be made at the desired pressures.

When it was required to work in the higher pressure range, the mercury was brought down as far as possible in A, valve F opened and the storage cylinder heated above the temperature of the condenser and compressor. CO<sub>2</sub> then distilled into the apparatus.

### *The Experiments.*

Before starting measurements on CO<sub>2</sub> the apparatus was tested by measuring the influence of pressure on the dielectric constant of N<sub>2</sub> at 25°, 75° and 125° C. up to 150 atms. Results have already been published as the 29th Communication of the Van der Waals Fund.\*

Measurements with CO<sub>2</sub> were carried out at the following twelve temperatures: 25°, 30°, 31°, 32°, 40°, 50°, 75°, 100°, 125°, 140°, 145° and 150° C., thus including runs through the critical region, and slightly under and above the critical temperature. Pressures used were between 30 and 1000 atms.

The work was carried out in two stages, above and below 250 atms. This was necessary, as the variable condenser could not cover the complete range and a change in the fixed condensers had to be made.

The results are given in Table I and fig. 13. Not all the points have been plotted on account of their number. In the lower pressure range the results are shown on a larger scale, fig. 14.

The tables give the figures for temperature, pressure in international atmospheres, dielectric constant, and the Clausius-Mosotti expression for those points where isotherm data were available (density expressed in Mols./cc.).

The accuracy in the dielectric constant is  $\pm 0.0007$ . The isotherm data have been taken from AMAGAT as being the most extensive available.

Above 100° the Clausius-Mosotti constant has not been given as the temperature-interpolation for the isotherms was too large, nor below 100 atms., as the change of density with pressure is too rapid. Some points measured by NIJHOFF, GERVER and MICHELS,† agree with AMAGAT's figures with an accuracy of  $\frac{1}{2}$  per cent. or better. This accuracy, together with the reliability of the interpolation, limits the accuracy of the constant where given.

It can be seen from the figures that, within the experimental error, there is no effect of temperature on the Clausius-Mosotti constant.

With increasing pressure the Clausius-Mosotti constant shows a tendency to decrease.

\* MICHELS and MICHELS. 'Phil. Mag.', vol. 13, p. 1192 (1932).

† 'Proc. Acad. Sci. Amst.', vol. 33, p. 72 (1930).

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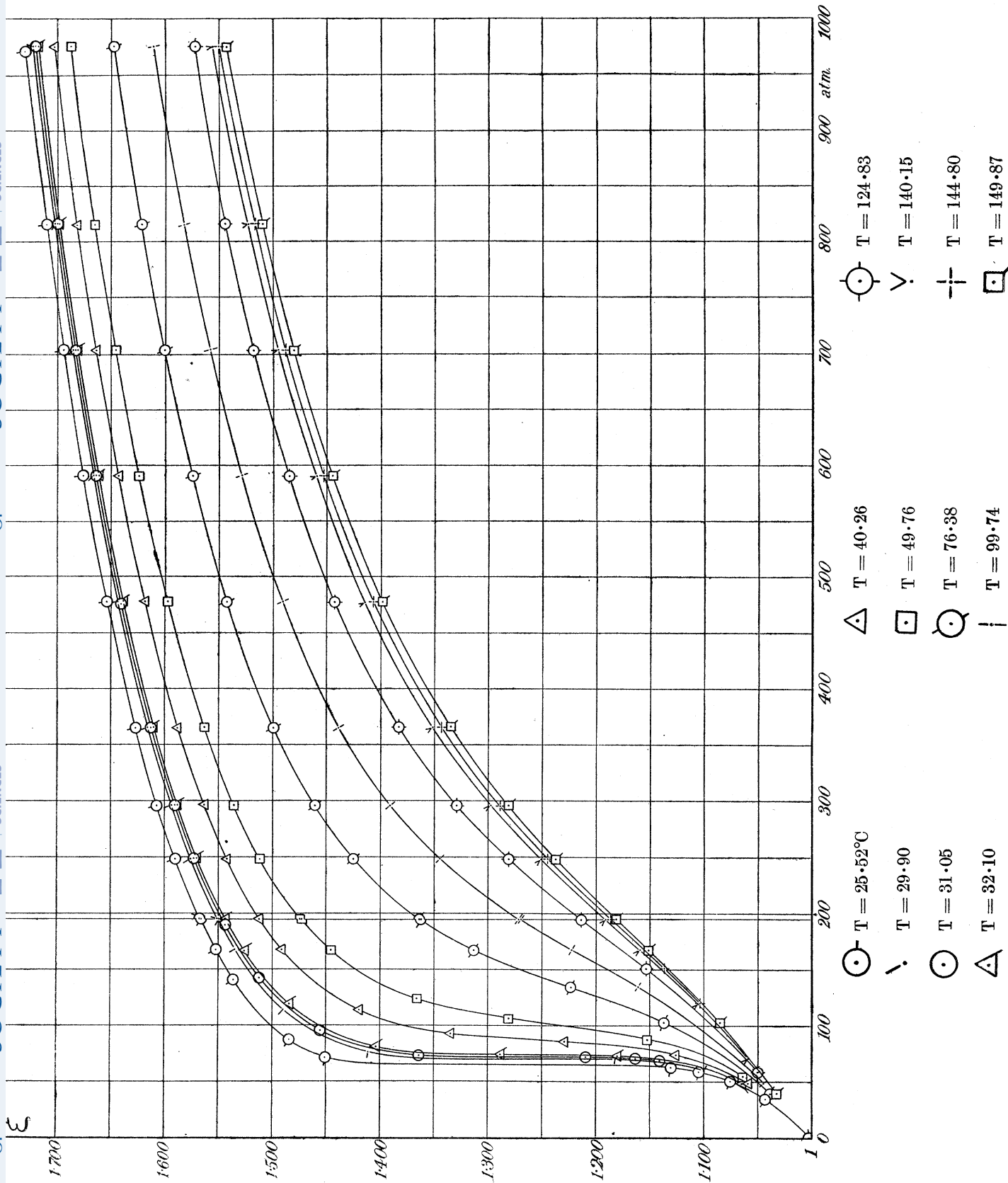


FIG. 13.

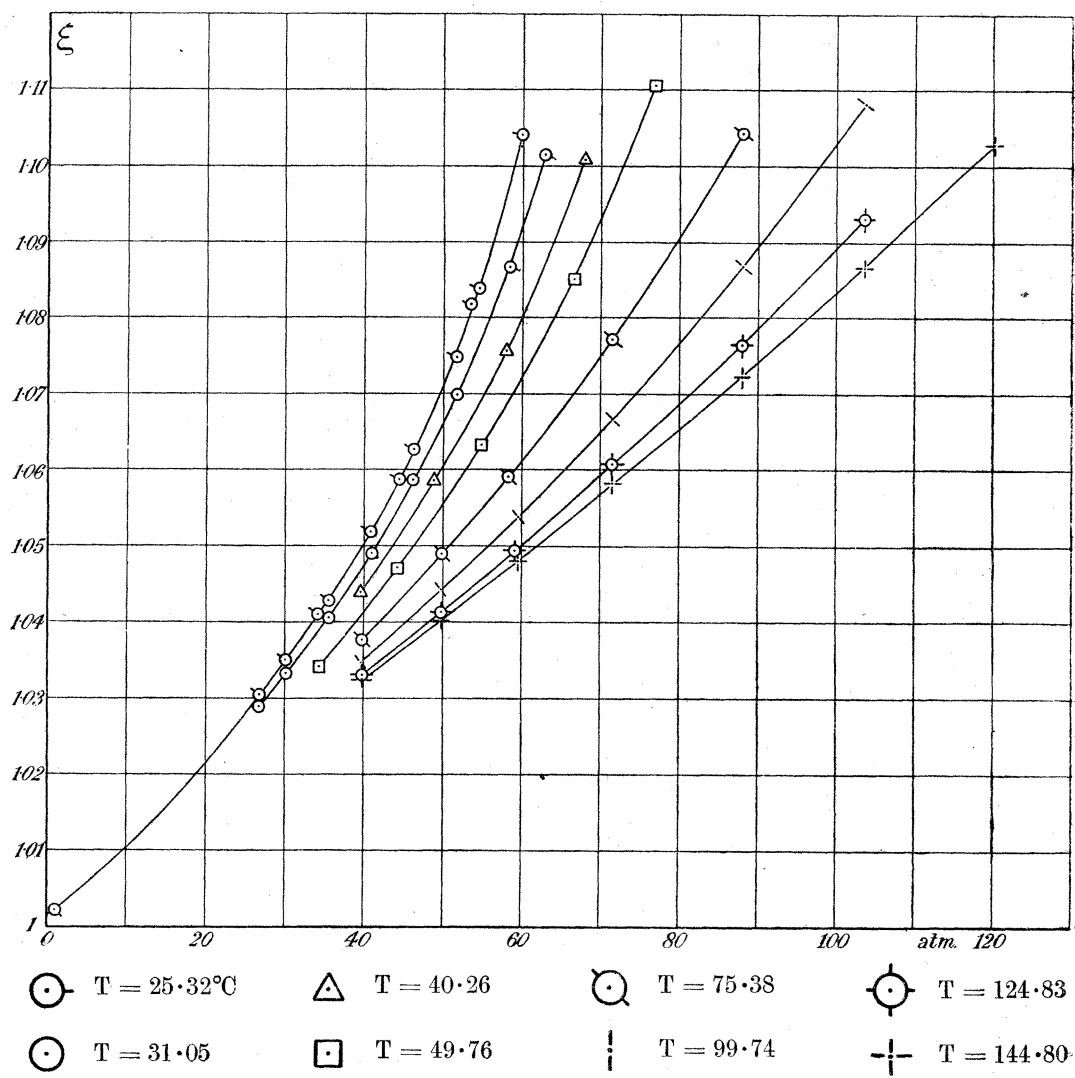


FIG. 14.

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TABLE I.

T.	$p_{\text{Atm.}}$	$\epsilon$ .	$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d}$ .
25.37	1.03	1.0009	
25.32	26.76	1.0306	
25.32	30.05	1.0353	
25.32	34.31	1.0413	
25.32	35.44	1.0430	
25.32	40.84	1.0521	
25.32	44.36	1.0590	
25.32	46.21	1.0629	
25.32	51.67	1.0751	
25.32	53.74	1.0821	
25.32	54.48	1.0842	
25.32	59.74	1.1045	
25.32	60.30	1.1074	
25.32	60.53	1.1099	
25.32	60.76	1.1099	
25.32	63.52	1.1301	
25.32	71.15	1.4504	
25.33	87.60	1.4828	
25.33	114.26	1.5132	7.72
25.33	141.00	1.5346	7.69
25.32	167.32	1.5511	7.68
25.32	194.41	1.5644	7.67
25.32	220.97	1.5765	7.67
25.32	247.75	1.5873	7.68
25.33	194.49	1.5658	7.68
25.33	247.80	1.5886	7.70
25.33	295.27	1.6054	7.69
25.33	364.84	1.6257	7.67
25.33	476.50	1.6523	7.66
25.33	588.23	1.6739	7.66
25.33	700.03	1.6921	7.65
25.33	812.15	1.7085	7.65
25.33	966.58	1.7285	7.63
25.34	194.49	1.5663	7.68

TABLE II.

T.	$p_{\text{Atm.}}$	$\epsilon$ .	$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d}$ .
29.90	1.035	1.0013	
29.90	36.66	1.0409	
29.90	47.78	1.0594	
29.90	59.44	1.0870	
29.90	61.11	1.0993	
29.90	66.41	1.1251	
29.90	70.75	1.1815	
29.90	71.24	1.3606	
29.90	76.47	1.4098	
29.90	87.57	1.4465	
29.90	114.23	1.4885	7.70
29.90	140.09	1.5140	7.66
29.89	167.72	1.5332	7.65
29.89	194.42	1.5487	7.65
29.89	221.02	1.5615	7.67
29.89	247.63	1.5730	7.68

TABLE II (continued).

T.	$p_{\text{Atm.}}$	$\epsilon$ .	$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d}$ .
29.90	194.49	1.5502	7.67
29.90	247.82	1.5749	7.67
29.90	295.26	1.5927	7.69
29.90	364.83	1.6142	7.67
29.87	476.50	1.6419	7.66
29.90	588.20	1.6646	7.66
29.90	700.02	1.6837	7.66
29.90	812.15	1.7005	7.66
29.90	970.46	1.7213	7.63
29.90	194.48	1.5501	7.67

TABLE III.

T.	$p_{\text{Atm.}}$	$\epsilon$ .	$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d}$ .
31.05	26.71	1.0291	
31.05	30.02	1.0334	
31.05	35.41	1.0408	
31.05	40.83	1.0494	
31.05	46.23	1.0590	
31.05	51.67	1.0703	
31.05	58.29	1.0871	
31.05	62.66	1.1018	
31.05	67.67	1.1266	
31.05	68.60	1.1328	
31.05	69.53	1.1406	
31.05	70.46	1.1501	
31.05	71.39	1.1626	
31.05	72.32	1.1851	
31.05	72.73	1.2087	
31.05	72.83	1.3088	
31.05	73.19	1.3393	
31.05	74.12	1.3629	
31.05	76.93	1.3916	
31.05	81.60	1.4159	
31.05	95.65	1.4540	7.65
31.05	119.09	1.4881	7.65
31.05	142.54	1.5105	7.66
31.04	165.98	1.5281	7.66
31.04	189.45	1.5424	7.64
31.04	212.89	1.5546	7.68
31.04	245.72	1.5691	7.69
31.04	194.49	1.5464	7.68
31.04	247.82	1.5715	7.70
31.04	295.26	1.5892	7.69
31.04	364.83	1.6114	7.67
31.04	474.51	1.6393	7.67
31.04	588.22	1.6624	7.66
31.04	700.03	1.6816	7.67
31.04	812.16	1.6984	7.66
31.04	970.46	1.7194	7.63
31.04	194.49	1.5464	7.68

TABLE IV.

T.	$p_{\text{Atm.}}$	$\epsilon$ .	$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d}$ .
32.08	39.68	1.0475	
32.08	48.85	1.0641	
32.10	57.96	1.0855	
32.10	67.45	1.1231	
32.10	70.46	1.1421	
32.10	73.25	1.1792	
32.10	74.19	1.2158	
32.10	74.46	1.2509	
32.11	74.63	1.2872	
32.11	75.08	1.3270	
32.10	76.94	1.3671	
32.11	81.63	1.4020	
32.11	95.69	1.4463	
32.11	119.14	1.4829	7.67
32.11	142.59	1.5064	7.68
32.11	166.03	1.5243	7.67
32.11	189.49	1.5394	7.69
32.11	212.95	1.5519	7.69
32.11	245.78	1.5669	7.70
32.10	194.50	1.5422	7.69
32.10	247.82	1.5685	7.71
32.10	295.27	1.5868	7.69
32.10	364.85	1.6090	7.68
32.09	476.51	1.6327	7.67
32.10	588.23	1.6600	7.67
32.09	700.04	1.6797	7.66
32.10	812.17	1.6968	7.66
32.09	970.49	1.7178	7.63
32.10	194.49	1.5423	7.69

TABLE V.

T.	$p_{\text{Atm.}}$	$\epsilon$ .	$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d}$ .
40.26	39.59	1.0441	
40.29	48.78	1.0589	
40.26	57.90	1.0760	
40.27	67.69	1.1013	
40.26	74.24	1.1252	
40.26	81.71	1.1707	
40.26	86.38	1.2289	
40.26	89.17	1.2771	
40.26	93.84	1.3334	
40.26	98.77	1.3666	
40.26	114.32	1.4184	7.81
40.26	141.07	1.4624	7.71
40.26	167.81	1.4899	7.69
40.26	194.50	1.5106	7.68
40.26	221.06	1.5270	7.68
40.26	247.81	1.5410	7.67

TABLE V (continued).

T.	$p_{\text{Atm.}}$	$\epsilon$ .	$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d}$ .
40.25	194.50	1.5120	7.70
40.25	247.90	1.5412	7.67
40.25	295.53	1.5618	7.67
40.25	364.93	1.5866	7.67
40.25	476.59	1.6171	7.64
40.25	588.30	1.6418	7.64
40.25	700.09	1.6625	7.64
40.25	812.22	1.6805	7.65
40.25	970.54	1.7021	7.61
40.25	194.60	1.5104	7.68

TABLE VI.

T.	$p_{\text{Atm.}}$	$\epsilon$ .	$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d}$ .
°			
49.77	34.18	1.0343	
49.76	44.24	1.0474	
49.74	54.78	1.0635	
49.76	66.49	1.0854	
49.75	76.64	1.1110	
49.76	87.76	1.1516	
49.76	93.09	1.1794	
49.76	97.90	1.2113	
49.75	101.59	1.2393	
49.76	106.93	1.2801	
49.76	114.35	1.3249	
49.76	124.50	1.3645	7.71
49.76	141.08	1.4046	7.73
49.76	167.81	1.4445	7.68
49.75	194.51	1.4718	7.67
49.75	221.08	1.4926	7.65
49.76	247.83	1.5093	7.64
49.76	194.60	1.4731	7.69
49.76	247.92	1.5102	7.65
49.76	295.36	1.5348	7.67
49.77	364.94	1.5626	7.66
49.76	476.60	1.5964	7.65
49.75	588.32	1.6228	7.64
49.76	700.13	1.6449	7.65
49.75	812.49	1.6638	7.65
49.76	970.56	1.6866	7.61
49.75	194.60	1.4731	7.69

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TABLE VII.

T.	$p_{\text{Atm.}}$	$\epsilon$ .	$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d}$ .
°			
75·39	39·79	1·0379	
75·39	49·79	1·0492	
75·39	49·79	1·0491	
75·39	58·18	1·0594	
75·41	71·29	1·0777	
75·39	87·75	1·1046	
75·39	103·26	1·1359	7·64
75·40	119·72	1·1780	7·67
75·39	134·69	1·2223	7·74
75·39	151·26	1·2706	7·73
75·38	167·76	1·3121	7·81
75·39	194·50	1·3613	7·76
75·39	221·06	1·3961	7·72
75·39	247·80	1·4238	7·71
75·37	194·60	1·3624	7·78
75·37	247·93	1·4237	7·71
75·37	295·35	1·4596	7·69
75·37	364·93	1·4980	7·69
75·37	476·58	1·5409	7·67
75·37	588·30	1·5731	7·67
75·37	700·11	1·5986	7·65
75·37	812·23	1·6199	7·64
75·37	970·54	1·6464	7·61
75·37	194·60	1·3621	7·78

TABLE VIII.

T.	$p_{\text{Atm.}}$	$\epsilon$ .	$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d}$ .
°			
99·74	39·53	1·0349	
99·74	49·59	1·0446	
99·74	59·36	1·0541	
99·74	71·28	1·0670	
99·74	87·39	1·0873	
99·74	103·25	1·1086	7·71
99·74	119·74	1·1342	7·71
99·75	134·70	1·1601	7·74
99·74	151·30	1·1906	7·73
99·74	167·83	1·2217	7·74
99·74	194·52	1·2695	7·75
99·74	221·09	1·3102	7·74
99·74	247·82	1·3437	7·74
99·70	194·63	1·2704	7·77
99·70	247·96	1·3438	7·73
99·70	295·42	1·3895	7·70
99·70	364·98	1·4375	7·68
99·70	476·60	1·4900	7·67
99·70	588·33	1·5274	7·66
99·70	700·15	1·5570	7·66
99·70	812·28	1·5812	7·65
99·69	970·60	1·6097	7·62
99·70	194·63	1·2701	7·76



TABLE IX.—125°.

T.	$p_{\text{Atm.}}$	$\varepsilon$ .
°		
124·83	39·71	1·0332
124·82	49·73	1·0415
124·82	59·02	1·0497
124·82	71·29	1·0610
124·82	87·75	1·0767
124·83	103·26	1·0934
124·83	119·74	1·1125
124·84	134·71	1·1311
124·86	151·31	1·1528
124·83	167·87	1·1762
124·83	194·54	1·2121
124·83	221·11	1·2473
124·83	247·85	1·2800
124·84	194·56	1·2123
124·83	247·94	1·2796
124·79	295·39	1·3282
124·80	364·98	1·3816
124·82	476·61	1·4413
124·82	588·34	1·4838
124·82	700·14	1·5167
124·86	700·15	1·5165
124·77	812·28	1·5434
124·77	970·59	1·5714
124·77	194·56	1·2123

TABLE X.—140°.

T.	$p_{\text{Atm.}}$	$\varepsilon$ .
°		
140·15	39·72	1·0330
140·14	49·74	1·0407
140·11	59·38	1·0484
140·02	71·30	1·0586
140·11	87·76	1·0733
140·16	103·27	1·0878
140·14	119·75	1·1046
140·18	134·72	1·1206
140·16	151·31	1·1393
140·16	167·87	1·1585
140·16	194·55	1·1899
140·16	221·12	1·2209
140·16	247·86	1·2502
140·09	194·66	1·1899
140·09	247·98	1·2503
140·09	295·46	1·2968
140·10	365·05	1·3511
140·10	476·65	1·4137
140·11	588·37	1·4588
140·10	700·18	1·4935
140·10	812·31	1·5220
140·10	970·63	1·5546
140·11	194·65	1·1904

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TABLE XI.—145°.

T.	$p_{\text{Atm.}}$	$\epsilon$ .
144·84	39·73	1·0327
144·80	49·74	1·0406
144·84	59·38	1·0484
144·81	71·30	1·0583
144·82	87·74	1·0726
144·84	103·26	1·0870
144·83	119·74	1·1031
144·83	134·71	1·1185
144·83	151·32	1·1366
144·84	167·88	1·1542
144·84	194·55	1·1857
144·84	221·11	1·2154
144·84	247·86	1·2442
144·72	194·66	1·1848
144·77	247·98	1·2432
144·74	295·44	1·2887
144·76	365·04	1·3427
144·77	476·71	1·4059
144·77	588·44	1·4519
144·78	700·25	1·4866
144·78	812·36	1·5156
144·78	970·65	1·5490
144·78	194·66	1·1851

TABLE XII.—150°.

T.	$p_{\text{Atm.}}$	$\epsilon$ .
149·87	39·63	1·0330
149·87	49·68	1·0405
149·87	59·38	1·0480
149·87	71·28	1·0578
149·87	87·76	1·0717
149·87	103·26	1·0856
149·87	119·74	1·1013
149·87	134·70	1·1161
149·87	151·31	1·1333
149·87	167·87	1·1512
149·86	194·55	1·1803
149·87	221·11	1·2091
149·86	247·86	1·2369
150·22	194·66	1·1793
150·22	248·00	1·2355
150·21	295·43	1·2800
150·21	365·02	1·3340
150·21	476·61	1·3976
150·22	588·34	1·4437
150·21	700·15	1·4796
150·22	812·28	1·5088
150·22	969·61	1·5426
150·24	194·68	1·1793

*Summary.*

The influence of pressure on the dielectric constant of carbon dioxide was measured at a frequency of 508 kilocycles using the heterodyne beat method.

Results are given for pressures from 30 to 1000 atmospheres at 25°, 30°, 31°, 32°, 40°, 50°, 75°, 100°, 125°, 140°, 145° and 150° C.

Where possible, the value for the Clausius-Mosotti expression has been calculated, and is found to be independent of temperature, and to show a tendency to decrease with increasing pressure.

A detailed description is given of the high pressure apparatus, the electrical circuit, and thermostatic and other devices used.