A DETERMINATION OF THE DIELECTRIC CONSTANTS OF FIVE GASES BY A HIGH FREQUENCY METHOD

By Edwin C. Fritts

Abstract

Dielectric constants of hydrogen, oxygen, nitrogen, air, and CO_2.—Special cylindrical gas condensers were constructed so as to have a minimum of solid dielectric in the field, and the small capacities were measured by the method of heterodyne beats, originally used by Hyslop and Carman. A photographic record of the beats on a moving film was secured, one side of the wedge slit being fastened to a tuning fork and the other to the diaphragm of a telephone actuated by the beats. The results reduced to 1 atm. at 0°C, accurate to about one per cent of the difference from vacuum, are: hydrogen 1.000263, oxygen 1.000507, nitrogen 1.000555, air 1.000540, and CO_2 1.000948. The values for N_2 were found to be independent of the frequency between 1230 and 600 meters, and to be proportional to the pressure from 44 to 69 cm. The values for air, N_2 and O_2 differ by 8 per cent from those of Boltzmann and of Rohmann.

THE initial object of the following investigation was to measure the magnetic susceptibility of oxygen. The general plan was to measure the change in frequency of an oscillating circuit when the pressure of the gas in the magnetic field of the circuit was changed. In the development of the method it was soon found that correction must be made for the distributed capacity of the coil used due to the change in the gaseous dielectric. The investigation was thus naturally turned first into determinations of the dielectric constants of gases as reported here, and the determination of the magnetic susceptibility of the gases is left for future investigation.

The method of determination of the change in frequency was based upon the heterodyne principle, which has been used for several years by Professor A. P. Carman and his students in this laboratory in measurement of dielectric constants.[1] There are two oscillating circuits, containing three-electrode valves. One circuit is used as a constant reference circuit. The second circuit contains air condensers, one of which can be altered in capacity by the change of the dielectric. The beat frequency between the two circuits gives a direct and exceedingly sensitive means of noting a change of frequency of the second circuit. The beat frequency can be adjusted in each case to that of a standard tuning fork by chang-

[1] W. H. Hyslop and A. P. Carman, Phys. Rev. **15**, 243, 1920; also theses and other unpublished MSS.

ing the capacity a known amount. Whiddington[2] used similar heterodyne circuits for the measurement of small displacements by measuring the change of capacity between two parallel plates when one plate was moved with respect to the other. Belz[3] has recently used Whiddington's method for the measurement of the magnetic susceptibility of certain salts.

The type of circuit used in the present investigation is shown at A and B in Fig. 1. The inductances L_a and L_b are wound in toroid form to eliminate stray fields. Two "Radiotron UV 202" power tubes are shown at PT_1 and PT_2. To prevent temperature variations about these tubes they were shielded with cardboard cases. The filament battery BA_1

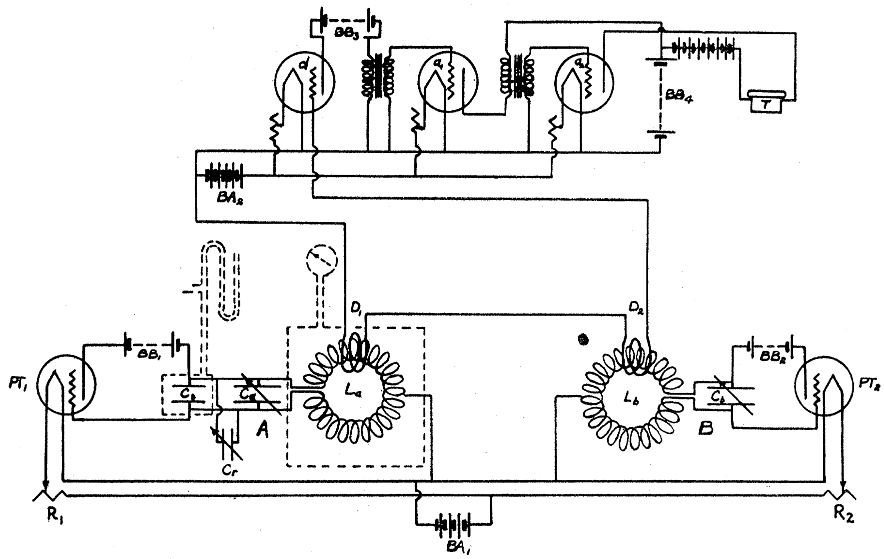

Fig. 1

consists of two sets of four storage cells in series connected in parallel, each cell having a capacity of 320 ampere hours. In the final experiments the resistances R_1 and R_2 were omitted, the e.m.f. of 8 volts at the battery being just sufficient to furnish the rated potential of 7.5 volts to the tubes. The plate batteries BB_1 and BB_2 are dry cell radio batteries each of 43 volts.

The beat frequency is produced by the use of two detector coils D_1 and D_2 which consist of five turns each wound loosely around L_a and L_b as shown. These coils are connected in series and to a detector and two stage amplifier, shown at the top of Fig. 1. The plate batteries BB_3 and

[2] R. Whiddington, Phil. Mag. **40**, 634, Nov. 1920.

[3] U. H. Belz, Phil. Mag. **44**, 479, 1922

BB_4 consist of 20 storage cells of small capacity giving an e.m.f. of 40 volts. As shown, an additional battery of this type is put into the plate circuit of the last amplifier. The output of the amplifier is connected to a Baldwin receiver T.

This method of producing the beat frequency between the two circuits eliminates the variations in the frequency of circuits A and B due to variations in the detector system and makes possible the operation of the system at a distance so that no variations are produced by the movements of the operator. The circuits A and B were enclosed in a

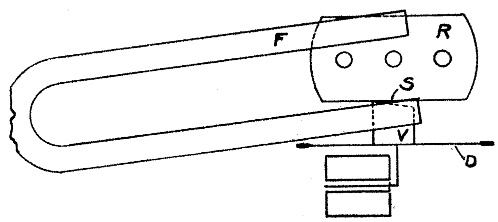

Fig. 2

wire cage supported on strong wall brackets and were sufficiently separated so that there was practically no coupling between the two circuits. It was found that the smaller the dimensions of the batteries BB_1 and BB_2 the less was the change of frequency due to a change in the position of external objects. In the experiments no trouble of this sort was appreciable but as a safeguard the compact radio dry batteries were used because of their size.

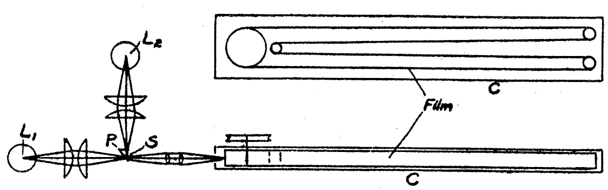

Fig. 3

A detail of the mounting of receiver T is shown in Fig. 2. The diaphragm D carries a light vane V which forms with the razor blade R a wedge shaped slit S. A tuning fork F forms a similar wedge at the other end of the slit. Thus the vane, the tuning fork and the razor blade form the sides of a triangular slit S, the razor blade forming the upper side. S is strongly illuminated by the system shown in Fig. 3, the low voltage concentrated filament lights L_1 and L_2 each illuminating half of it.

From the condensing lenses the light from L_1 passes directly to the slit S while that from L_2 is reflected upon the slit by a right angle prism P. The camera is a box about 4 ft long and 8 by 3 inches in cross-section. It contains adjustable rollers so that a continuous moving picture film about three feet or more long can be mounted in it. The slit is placed with its length at right angles to the direction of motion of this film and an image of the slit is focused on the film by a lens as shown. To enable the operator to limit the exposure to the length of the film a shutter (not shown in the diagram) was placed immediately in front of the camera. The camera was driven by a spring motor of very constant speed. As the tuning fork and diaphragm vibrate, the slit is periodically altered in length and the resulting exposure is shown in Fig. 4 which is a print taken from a portion of one film. The six white portions of Fig. 4 indicate portions of six exposures produced on the film. In each exposure the

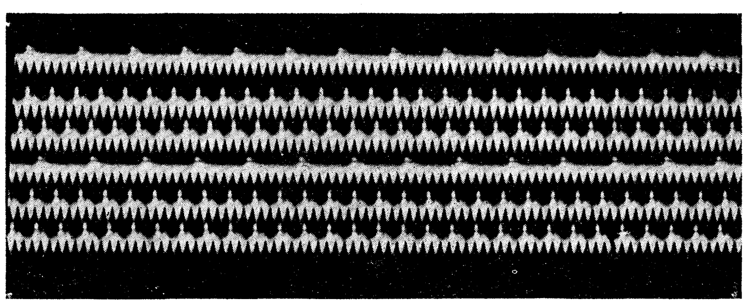

Fig. 4

record of the tuning fork is that with the finer teeth shown at the bottom of the exposure. The record of the vibrations of the diaphragm is at the top of the exposure. The record of the tuning fork is used as a measure of time in the determination of the frequency of the vibrating diaphragm as will be explained later. The frequency of the diaphragm thus recorded is the beat frequency between circuits A and B. If the frequency of circuit B is kept at a constant value then any change in the frequency of circuit A is equal to the change in the beat frequency which after being recorded can be measured against the tuning fork frequency.

The condenser C_1 was used in three different forms, the first of which is shown in Fig. 5. Six coaxial cylinders form the plates. Each end of each cylinder is cut away to a depth of one quarter of one inch along two opposite quadrants. Two brass plates were made and concentric grooves cut in them to fit the cylinders. These plates were then cut into quadrants A and B and the condenser was assembled and soldered together.

Alternate cylinders were soldered into alternate quadrants; the bottom quadrants were secured by screws, one of which is shown at *D*, to hard rubber quadrants and these quadrants were secured by screws, one of which is shown at *E*, to a marble base. This construction was adopted to give a rigid condenser in which there was little solid dielectric in

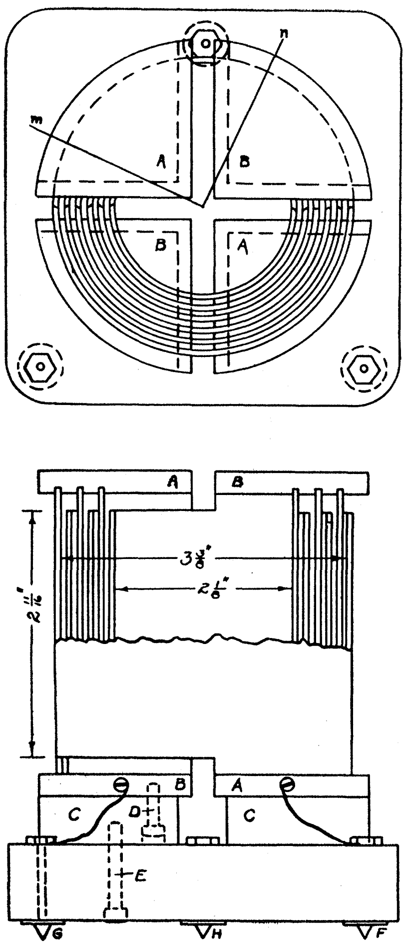

Fig. 5

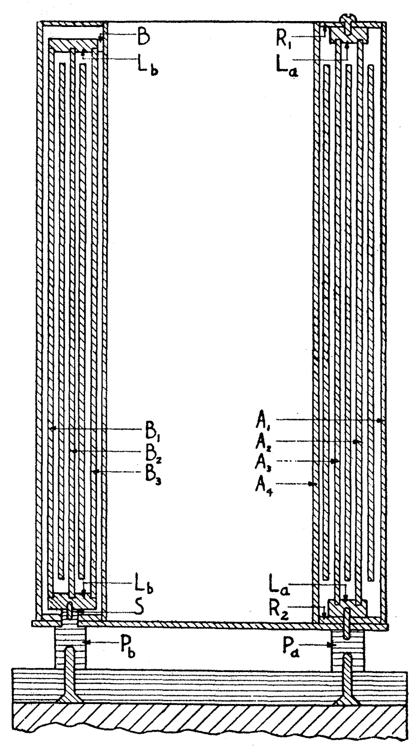

Fig. 6

the field. The condenser was carried on three points *F*, *G*, and *H*, and connections were made through the points *F* and *G*.

The second and third forms of the condenser C_1 will be denoted by C_2 and C_3, respectively. The results to be given later seem to indicate that the measurement with C_1 was subject to a small error due to a stray field between the bottom quadrants through the hard rubber and the marble. For this reason C_1 was modified into the form C_2 and a new and larger condenser C_3 was made, so as to eliminate this error. A section through C_2 along the line *mn* (Fig. 5) is shown in Fig. 6. In this form the quadrants are mounted on hard rubber posts P_a and P_b which carry also, below the quadrants, a brass plate C connected to the lower quadrants B (Fig. 5). The quadrants A are insulated from the first set by shoulders S turned on the posts P_2. Small screws are used to secure the quadrants to the posts. Around the whole is placed a metal cap D also connected to the quadrants. In this way the whole field is confined within the condenser and only the small portion of solid dielectric at S and B is in the field. The third condenser C_3 was very similar to C_2 but with larger capacity.

These condensers C_1, C_2 or C_3, were enclosed in a glass bell jar and arranged so that the identical placing of the condenser could be secured. In the base of the bell jar was placed a junction of a thermocouple and a gas outlet.

Capacity C_a (Fig. 1) was a high grade circular-plate variable condenser constructed of cast brass plates. By several calibrations the relation between the reading in degrees and the capacity of such condensers has been shown to be strictly linear over the greater part of the scale. Capacity C_b (Fig. 1) was identical with C_a and C_r was similar to C_a, differing only in size. C_r was fitted with a slow motion screw. A mirror was attached and small angular displacements were measured by a telescope and scale.

C_r and C_1 were calibrated in terms of degrees along the straight line portion for C_a. For purposes of calibration C_1 and C_a are both connected as indicated by A (Fig. 1), C_a being set near the lower end of its linear calibration. Circuit B was then adjusted to the same frequency as circuit A by finding the point of zero beats between the two circuits. This method of adjustment was extremely accurate since the beats could be decreased to the point where they could be easily counted audibly before they died out, a fact probably due to the coupling between the circuits being so small that there was little tendency for the circuits to be forced into the same frequency by their mutual inductance. After this adjustment of circuit B, condenser C_1 was disconnected by removing the leads in the base of C_1 from the quadrants and C_a was readjusted until the circuits were again at the same frequency. In this manner only that portion of C_1 was removed from the circuit in which the dielectric was changed. The difference between the two capacities of C_a was then the capacity of C_1. The difference between the capacities of C_r when set at two points along its straight line calibration, was determined in the same way and the value of C_r per degree and in terms of degrees on C_a found. After these calibrations C_a was removed from the circuit.

C_2 was measured in the same way as C_1. In the case of C_3 the capacity was too large to permit direct substitution along the straight line portion for C_a and the calibration was carried out in the following manner. C_3 was connected in the circuit A and C_a set near the lower end of its linear calibration as before and the circuit B was brought to the same frequency. Then C_3 was disconnected and C_2 connected into the circuit. C_a was then re-adjusted as before until the circuits were at the same frequency. The capacity change in C_a was then equal to the difference between C_3 and C_2, and C_3 was taken as the sum of this value and C_2.

These capacity measurements were checked by a capacity bridge method and the values agreed within about 1 per cent.

The bell jar containing the condenser C_1 was connected through the gas outlet to a system of stop cocks leading to an oil pump and a gas reservoir. Commercial gases were used, supplied in the usual high pressure cylinders. The reservoir was constructed from a two foot length of four inch steam pipe fitted with caps on each end. The gases were passed through a calcium chloride tube about three feet long into the reservoir until the pressure was sufficient to produce, after expansion into the evacuated bell jar, a final pressure equal to that of the atmosphere. Pressures were read on an open manometer M. The temperature was determined by the thermocouple and a potentiometer. The temperature was always found to be equal to that of the room except for a small momentary change after expansion.

The procedure in the experiment was as follows. The pressure in the bell jar was reduced to less than 1 mm as measured on a small closed manometer in J and the frequency of the circuit B was adjusted to a value about 100 cycles greater than that of circuit A. After closing the stop cock and stopping the motor used to drive the pump, a record n_1 was made of the beat frequency. By opening the second stop cock the gas was allowed to expand into the bell jar and a second record n_2 was made. C_r (Fig. 1) was then decreased by about one or two degrees and a third record n_3 was made. The total time for making the three exposures was about twenty five seconds. The initial and final readings of the telescope, d_1 and d_2 and the difference from atmospheric pressure were noted. The temperature was measured and the barometric pressure read.

The film on which the records were made was driven at a very constant speed. This made possible a very easy method of counting the beat frequencies n_1, n_2, and n_3. Twenty five cycles on the tuning fork record were counted and a pair of dividers set to this measure. The dividers were then used to lay off four hundred cycles by intervals of twenty-five, beginning at a point where a peak on the tuning fork record was coincident with a peak on the beat record. The number of beat cycles in this length were then counted in a similar manner, estimating to one tenth of a cycle. By keeping the beat frequency small this method was very accurate and by checking from time to time the method of counting was found to be exact.

In the equation

$$dn/dC = n/2C \tag{1}$$

dn is proportional to dC if n and C are not appreciably altered.

The change of capacity due to the change of dielectric from a vacuum to a gas is equal to $(K-1)\ C_1$ where K is the dielectric constant of the gas. Due to the change in capacity by the introduction of the gas we have the change of frequency n_g equal to $n_2 - n_1$, and due to the change in capacity in C_r we have the change n_c equal to $n_2 + n_3$, since the beat frequency was carried through zero to a value in the opposite direction. This method was adopted in the change of C_r to produce a change which could be accurately measured while keeping the beat frequency down to a value which could be easily counted.

By equation (1) we have

$$(K-1)C_1/C_r = n_g/n_c \tag{2}$$

where K is the dielectric constant of the gas at the temperature and pressure of the experiment. The dielectric constant of a gas, as will be seen by results to be given later, is directly proportional to the pressure. Assuming that the temperature effect is only one of density we may, therefore, reduce K to its value at one atmosphere and zero degrees by dividing the right hand member of Eq. (2) by P_0 where

$$P_0 = (273/T)\ (P/76) \tag{3}$$

P being the pressure in cm of mercury and T the absolute temperature of the gas. The value of C_r in Eq. (2) was determined by the equation

$$\Delta C_r = (d_1 - d_2)\ 180R/2\pi D \tag{4}$$

where R is the value of C_r per degree in degrees on C_a, and D the distance between the telescope and scale. For convenience in calculating, Eq. (2) was used in the form

$$\frac{(K-1)\ C_1}{\Delta C_r'} = \frac{\Delta n_g}{\Delta n_c/(d_1 - d_2)} \tag{5}$$

where

$$\Delta C_r' = \Delta C_r/(d_1 - d_2)$$

or the change of the capacity of C_r per cm deflection in the telescope. It was further assumed that variations in the values of $\Delta' n_c$ throughout the experiments in which circuit A was unaltered were experimental rather than variations in the circuit itself and the mean of all such values was used in each calculation. Since in Eq. (2) Δn_g and Δn_c appear only in the ratio between the two quantities it is immaterial whether these quantities are expressed in cycles per second or involve some other unit of time. The tuning fork had a frequency of 512 cycles per second. It was found much more convenient to count the records by hundreds and therefore all values given for the changes in frequency in the following data are per 400 cycles of the tuning fork rather than per 512. The final equation for determining the dielectric constant is

$$K = 1 + \frac{\Delta n_g \times 180 \times 76 \times RT}{2\pi D \times 273 P \times [\Delta n_c/(d_1 - d_2)]\, C_1}. \qquad (6)$$

The following precautions were followed in the experimental work.

1. Considerable trouble was experienced due to changes in the filament temperatures of the oscillating tubes. This trouble was removed by eliminating as far as possible, all contacts in the filament circuits and soldering as many of those which remained as was convenient. It was for this reason that resistances R_1 and R_2 (Fig. 1) were removed.

2. Variations probably due to (1) were originally ascribed to the plate batteries. Although such variations probably did not originate in the plate batteries, yet the size of these batteries determined quite largely the magnitude of the variations. When, for instance, small storage batteries were replaced by the equivalent number of dry cells, which occupied much more room, the variations in frequency were increased several fold. For this reason the radio batteries referred to above were used. It was also found better to keep these batteries at some distance from the wire net by which the system was shielded.

3. The variable condensers C_a and C_r were first equipped with flexible cables connecting the rotating plates with the binding posts. Using them in this form seemed to give slight variations in the measurement of the capacities C_1 and C_r but after rigid sliding contacts were substituted for the cables such measurements could be repeated as closely as C_a could be read.

4. The insulating property of each of the condensers C_1, C_2, and C_3, was tested by charging and connecting with an electroscope and noting the rate of discharge. It was found that no noticeable collapsing of the leaves occurred during five minutes.

5. No noticeable advantage was gained by shielding the oscillating circuits but this precaution was carefully followed. The detector system

was not shielded but no trouble was experienced in using it in this manner. This system was placed several feet from the cage containing the oscillating circuits.

6. Upon request the manufacturers furnished a statement in which a purity of 99 per cent was claimed for the nitrogen, oxygen and hydrogen used. The carbon dioxide was obtained in the commercial cylinders and was carefully dried. The air was taken from the air mains and carefully dried.

7. Before any experiments were performed time was allowed for the tubes to come to a uniform temperature. All doors and windows to the room were kept closed so that no air currents were present.

8. The motor driving the air pump was stopped before each experiment.

9. Experiments were performed to test for changes in frequency due to changes in the bell jar system or due to any drift in the beat frequency. These experiments showed such variations to be not greater than 0.2 of a cycle per 400 cycles of the tuning fork.

10. In changing from one gas to another the reservoir and drying tube were pumped out to about 2 mm pressure, filled to atmospheric pressure with the new gas then again pumped out and refilled before any data were taken.

Experimental Results

Table I gives a set of readings in detail so as to show the character of the measurements.

TABLE I

Run No. 1, Nitrogen

$C_1=77.5°$ on C_a; Total cap. = 675 m.m.f. (approx.); $D=268.6$ cm; $\lambda=393$ meters.

P	T	Δn_g	$\Delta n_c/(d_1-d_2)$	K at 1 atm. and 0°C
		C_r set at 130°		
74.9	296°K	99.0	52.1	1.000551
74.9		99.0	51.8	1.000551
74.9		100.2	53.2	1.000556
74.7		96.5	51.4	1.000538
74.7		96.5	51.4	1.000538
74.57		97.5	51.9	1.000545
74.57		98.0	51.6	1.000547
		Means:	52.0	1.000547
		C_r set at 135°		
75.8	296	97.2	51.35	1.000537
74.5		95.5	52.3	1.000537
75.0		99.0	51.6	1.000553
74.6		97.9	51.7	1.000550
		Means:	51.74	1.000554
		C_r set at 150°		
75.1	296	93.8	48.7	1.000554
			Grand mean:	1.000546

TABLE II

Summary of all sets of readings

Number of run	Gas	No. of readings	Pressure mean	Wave-length λ in meters	K reduced to 0°C and 1 atm.
1	N_2	12	74.9 cm Hg	393	(C_1)(1.000546 $\pm .0^5 62$)
3	N_2	15	74.3	593	1.000555 $\pm .0^5 20$
4	N_2	9	74.2	1230	1.000556 $\pm .0^5 25$
5	N_2	1	75.65	593	1.000558
	N_2	1	62.5	593	1.000558
	N_2	1	48.2	593	1.000557
2	O_2	5	74.8	393	(C_1)(1.000490 $\pm .0^5 54$)
6	O_2	7	75.0	593	1.000505 $\pm .0^5 26$
7	O_2	1	74.2	593	1.0005111
	O_2	1	48.4	593	1.000512
	O_2	1	33.7	593	1.000512
8	H_2	5	74.7	605	1.000263 $\pm .0^5 15$
9	CO_2	7	73.0	605	1.000948 $\pm .0^5 16$
10	Air	6	75.0	605	1.000540 $\pm .0^5 11$

Runs No. 1 and 2 were made using C_1, and are given merely for comparison with the later data. It will be seen that the later runs made using C_2 and C_3 give values about two per cent higher than were obtained in Runs 1 and 2. This difference is ascribed to the stray field through the hard rubber and marble base of C_1 in which the dielectric was not changed and for this reason the values obtained in runs 1 and 2 are not included as a part of the final values. It was also found that the values obtained in the later runs check among themselves more closely than do the values from runs 1 and 2. The mean deviations from the mean for each run is given in the last column and is seen to be much greater for runs 1 and 2.

In run 3 data were taken with both condensers C_2 and C_3. Where C_2 was substituted for C_3 a sufficient portion of C_a was added to the circuit to bring the frequency to the same value as when C_3 was used. The means of 11 readings with C_3 and of 4 readings with C_2 check exactly. This fact is conclusive evidence that the values are independent of the condenser, and since the solid dielectric in the case of condenser C_2 contains perhaps three times as great a part of the total capacity of the condenser as in the case of C_3, it is also evident that no appreciable error is introduced by this solid dielectric. Run 4 was made under the same conditions as run 3 except that the wave-length was changed by increasing the number of turns on the coils L_a and L_b (Fig. 1). It is seen that the same values are obtained at this wave-length as are obtained at approximately one half the wave length; it is therefore evident that there is no variation of the dielectric constant with frequency over this range. It is perhaps well also to mention here that in these experiments the changes in frequency were so small that it was found advantageous to take all beat frequency records on the same side of the point of resonance. This is also a check on the general method used where in changing C_r the beat frequency was carried through its zero value to a point on the opposite side. Runs 5 and 7 show that the dielectric constant is strictly proportional to the pressure for pressures less than one atmosphere.

In considering the absolute values in relation to the values given by previous investigators the following facts are to be noted.

1. The values of Boltzmann for carbon dioxide and hydrogen are checked to less than one half of one per cent.

2. The values for nitrogen, oxygen and air are lower than the values of Boltzmann and Rohmann with the ratios given in Table III.

TABLE III

Values of $K-1$

Gas	Boltzmann (I)	Rohmann (II)	Fritts (III)	Ratio (II/III)
Air	.000590	.000580*	.000540	1.074
CO_2	.000946	.000989	.000948	1.04
N_2	———	.000606	.000555	1.090
O_2	———	.000547	.000507	1.08
H_2	.000264	.000282	.000263	1.072

Since the ratios in Table III are all near the same value and the values of Boltzmann for carbon dioxide and hydrogen are checked so closely the present results seem to indicate that the value for air of 1.000580 which has been assumed by Rohmann should be replaced by 1.000540.

Errors. Of the quantities involved in the Eq. (6) R, C_1, C_2 and C_3, and D were measured and checked with a high accuracy. The temperature was measured to one degree and is therefore subject to a maximum error of about 0.3 of one per cent. The pressure P was measured to one mm of Hg and is subject to a maximum error of about 0.13 per cent. The values of d_1-d_2 are subject to an error not greater than 0.2 of one per cent. The errors in n_g and n_c are of the same order as the above errors.

In conclusion, the author wishes to thank Dr. Jakob Kunz under whose direction the investigation was carried out. The author is also grateful to Professor A. P. Carman for the helpful suggestions which he has made with regard to the work.

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UNIVERSITY OF ILLINOIS,
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* In order to check the values of Klemençiç more closely this value for air was assumed by Rohmann.

[4] Received September 22, 1923—Ed.

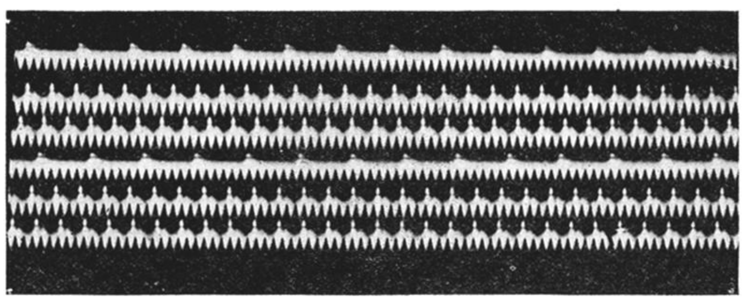

Fig. 4