The Dielectric Constants of Eight Gases

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The dielectric constants of eight gases have been measured by a heterodyne beat frequency method. Special precautions were taken to improve minor defects in the equipment which are believed to have contributed principally to the difference in average values obtained by other observers where these differences were incompatible with the self-consistency of the individuals' data. Data on helium, neon, argon, hydrogen, oxygen, nitrogen, carbon dioxide, and air are given and compared with the results of numerous other observers.

INTRODUCTION

VALUES of the dielectric constants of gases have been of interest to both physicists and chemists over a long period of years, and many experimental methods for making such measurements have been devised. These methods of measurement may be roughly classified as static methods and high frequency methods. With either method the dielectric constant of the gas is determined from a change in capacity of a condenser which may be immersed in the gas at various pressures. In the case of high frequency measurements the technique usually employed is to determine the change in frequency of a resonant circuit when the gas pressure surrounding a condenser is changed, or to determine the change in value of an auxiliary condenser in a resonant circuit to maintain the frequency constant as the gas pressure is changed. The usual procedure for making either of these types of measurements is to make the condenser immersed in the gas a part of the resonant circuit of one oscillator in a beat frequency circuit. The obvious advantage of this system is that it permits the comparison of two high frequencies so that a small difference between two large numbers is readily observed.

In nearly all cases of the measurement of the dielectric constants of gases the experimenters started by measuring air, and later they turned their attention to the particular gas or gases in which they were basically interested. Consequently, more measurements on the value of air are in the literature than for any other gas.

The senior author started a study of the measurements on dielectric constants primarily to determine whether there was a marked difference between values obtained by static techniques and by high frequency techniques. No such significant difference was observed, but it was noticed that the self-consistency in most individuals' sets of data was good, whereas the differences in average values between observers was unexplainably large. It was also noticed that much of the work done at high frequencies did not employ entirely modern techniques in the design of the oscillating circuits and in the isolation of the circuits so that they could not couple.

Consequently, experimental work was started by the senior author and Howard L. Schultz to see if the application of good high frequency technique would produce more reliable results. Data obtained by these observers were published in 1936 (11).†

Later the experimental work was re-started with the aid of Carl Seddon. A number of supposed refinements were introduced in the circuits and in the technique employed but the results obtained on air differed from those obtained with Schultz. In other words, the data obtained with Schultz and that obtained with Seddon were like that of previous observers—very self-consistent, but in disagreement between the two sets of data.

The senior author then started work with Donald L. Woernley and carried through extensive modifications of details of the equipment and technique. In general, the data obtained by Woernley were in agreement with those obtained by Seddon. The improvement in consistency be-

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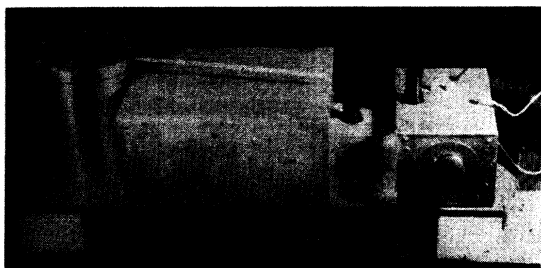† References are given at the end of this article in the Bibliography.

FIG. 1

tween the data of these observers indicates that the desired reliability is obtained by special care with regard to several minor details of the equipment and the procedure.

EXPERIMENTAL TECHNIQUE

The general technique employed by Schultz (11) was used throughout. The standard high frequency was obtained by the demodulation of a radio broadcast signal after the manner described by Schultz (30). The oscillator circuit in which the variable condenser was placed was a so-called electron coupled oscillator in which the resonant circuit uses the screen grid of a pentode as the plate and the output signal is taken from the plate itself. This resonant circuit was adjusted to zero beat with a standard frequency with the test condenser evacuated. The difference of frequencies resulting from the admission of gas to the test condenser was measured by recording the beat frequency with a string oscillograph. A standard audiofrequency was recorded on a second string of this oscillograph simultaneously.

The following items are the principal ones about which excessive care appears to make the necessary difference regarding the reliability of the data.

It is desirable to make the case of the condenser of very heavy material to avoid minute changes in dimensions caused by pressure changes inside of this case as the gas is admitted. Changes caused by this effect were further reduced by using a perforated shield inside of the outer case.

It is also necessary to take precautions to keep the temperature of the test condenser and its case constant, not only to simplify the problem of pressure and temperature measurements, but also to prevent changes in mechanical dimensions

of the condenser and its case. This problem was solved by building the test condenser external to the shield enclosing the oscillator since temperature difficulties would otherwise arise caused by the stabilization of the oscillator temperature above that of the room in which the gas supply is kept.

Another problem arises from the fact that it is difficult to build a condenser in which no part of the capacity is so located that it cannot be affected by the change in pressure of the gas. This problem is inherent since it is necessary to use solid insulating material to support the live plates and to surround the lead from the live plates as it comes through the shield and outer casing. It is possible, however, to take data under sufficiently varied conditions so that the unchanging part of the capacity can be eliminated from the calculations. It is, nevertheless, desirable to keep this unchangeable capacity as small as possible in order to improve the over-all reliability of the data.

Figure 1 shows the exterior appearance of the apparatus directly associated with the variable frequency oscillator in the latest version of this equipment. At the left we see a steel cylinder with a wall $\frac{3}{4}''$ thick and with $1''$ ends. It was tooled from a solid piece of steel. Inside this cylinder is a second cylinder, this one being of brass with perforated walls and ends. Gas pressure is changed inside of the steel cylinder and so changes on both sides of the perforated brass cylinder. The latter, then, should not experience serious structural changes as the gas pressure changes. It serves as an unchanging electrostatic shield for the condenser located inside of it. The live plates of the multiple plate condenser are mounted on three isolantite pillars. The plates are arranged so that various numbers of them can be used without changing the amount of the capacity in the solid dielectric. Data taken with two sizes of the condenser permit us to determine the value of the non-effective part of the test condenser capacity—in our case it is approximately 8/10 of 1 micro-microfarad in comparison to a total capacity of approximately 647 micro-microfarads. All the parts of this condenser are gold-plated to establish fixed surfaces of high conductivity.

The large section in the center of the apparatus

is a shield box made of $\frac{3}{8}''$ aluminum. It contains vernier condensers and an inductance coil wound on an isolantite form. The small thermionic tube mounted on this section is a single-ended radio frequency pentode with the characteristics of sharp cut-off plate current. This type of tube permits all of the wiring to be in the shield beneath the tube, and at the same time all of the heat developed by the tube is external to the shield.

The final section of the apparatus is a buffer amplifier which effectively prevents coupling between the variable frequency oscillator and the source of fixed frequency. The buffer is tuned to the second harmonic of the oscillator to further reduce coupling and to double the beat note. The temperature of the entire room was held constant to ±0.1°C by automatic thermostatic control during the taking of a set of data.

DISCUSSION OF DATA

Table I is a summary of most of the values for air that are available. The value 1.000600 at the beginning was obtained by a high frequency method as was the value 1.000540 at the end. The value 1.000590 was found by Boltzmann (1) in 1874 and the second value of 1.000590 is attributed to Schultz as measured in 1934 and published in 1936. The closest agreement to the results of Seddon and Woernley is that obtained by Zahn (8), although a static value obtained by Tangl (12) is also very close.

Table II shows a summary of the data on nitrogen. It may be noted that except for the one very low value there is much better agreement among observers for nitrogen than for air.

TABLE I. 14 values for dielectric constant of *air* at N.T.P. arranged in order of magnitude.

Value	Year	Ref.	Value	Year	Ref.
1.000600	1922	6	1.000586	1885	2
594	1927	3	579	1929	23
592	1931	4	576	1931	18
591	1934	5	573	1908	12
590	1874	1	572	1924	8
590	1936	11	547	1928	10
589	1928	9	540	1924	7
			1.000580		Av.
1.000569			Hector and Seddon		
1.000567			Hector and Woernley		

The most recently published data for nitrogen are those obtained by Fox and Ryan (20) in 1939. Their value agrees closely with ours. Again it may be noted that the value of Zahn (8) lies close to these values.

Table III shows values for oxygen. Our value for oxygen is higher than three of the four values shown here, whereas our values for air and nitrogen were lower than those of many observers.

It may be of some interest to compute the

TABLE II. 10 values for the dielectric constant of *nitrogen* arranged in order of magnitude.

Value	Year	Ref.	Value	Year	Ref.
1.000590	1931	14	1.000581	1908	12
589	1931	16	581	1924	8
587	1913	13	579	1939	20
587	1931	18	573	1932	17
582	1934	27	555	1924	7
			1.000580		Av.
1.000581			Hector and Seddon		
1.000580			Hector and Woernley		

value of air from the values of nitrogen and oxygen already shown and that of argon given in Table IX. Table IV shows the results of such a computation. It can be seen that the value for air obtained by this computation lies within 5 points in the 4th place of the value obtained by direct measurement. This agreement is within the uncertainty which we place on any of these data.

Table V shows a summary of published values for the gas hydrogen together with the values obtained by us.

Table VI is a set of data for carbon dioxide. Measurements by Fox and Ryan in 1939 indicate that the dielectric constant of carbon dioxide shows an anomolous rise in the temperature region. 25 to 40 degrees. We have, therefore, shown here only such data of other observers as were taken near the temperature employed by us.

Table VII shows values for the gas helium. The first four are theoretical calculations. Three of the four are in fairly close agreement among themselves and also with the value obtained by extrapolating optical data (22). Our value is in fair agreement with the theoretical values and with the one obtained from the optical data. For a discussion of the theoretical values in Table VII see reference (31).

TABLE III. Dielectric constant of *oxygen* at N.T.P.

Value	Year	Ref.
1.000507	1924	7
507	1901	29
518	1924	8
547	1911	28
1.000520		Av.
1.000525		Hector and Seddon
1.000523		Hector and Woernley

TABLE IV. *Air* calculated from the measured values of its components (CO_2 and H_2O free).

Substance	Percent	Value	Contribution
Nitrogen	78.06	5796	4525
Oxygen	21.00	5233	1098
Argon	0.94	5451	51
			1.0005674
Measured value			1.0005669
			±10

TABLE V. Dielectric constant of *hydrogen* (H_2).

Value	Year	Ref.
1.000263	1924	7
264	1875	15
265	1924	8
273	1908	12
275	1934	26
1.000268		Av.
1.000271		Hector and Seddon
1.000272		Hector and Woernley

TABLE VI. Dielectric constant of *carbon dioxide* at N.T.P. (data taken at temperatures indicated).

Temp.	Value	Year	Ref.
22°C	1.000982	1926	19
25	983	1931	18
25	987	1934	26
23.9	994	1939	20
23.9	996	1939	20
	1.000988		Av.
23.9	1.000988		Hector and Woernley

Table VIII is a set of data for neon. Our value is somewhat lower than that of other observers.

Table IX is a set of values for argon. Again our value is relatively low.

The values in parentheses in Tables VIII and IX are from data given in references (24) and (25) after correction to our values for air and oxygen.

TABLE VII. Dielectric constant of *helium* at N.T.P.

Theoretical values

1.0000653 by	Atanasoff
691	Hassé
1.0000790	Hassé
715	Slater and Kirkwood
712	Av.

Experimental values—Ref.

1.0000693 From optical data		
1.0000740	1908	21
728	1934	26
720		Av.
1.0000684	Hector and Woernley	

TABLE VIII. Dielectric constant of *neon* at N.T.P.

Value	Year	Ref.
1.000148	1929	24 (based on air at
(139)		1.000589)
134	1934	26
1.000127		Hector and Woernley

TABLE IX. Dielectric constant of *argon* at N.T.P.

Value	Year	Ref.
1.000575	1927	25 (based on O_2 at
(550)		1.000547)
574	1929	24 (based on air at
(553)		1.000589)
550	1934	26
1.000545		Hector and Woernley

The more common impurities to be found in each of the rare gases are the other rare gases and nitrogen. Such impurities would, of course, tend to increase the measured values, especially for helium and neon. The three rare gases used by us were specially prepared and purified for these measurements by the Linde Air Company research laboratories, through the courtesy of Dr. Leo I. Dana.

Table X is a résumé of our data on all of the eight gases which we have so far measured. The second column shows the number of observations and the third column the temperature range at which the data were taken. The fourth column shows the smallest and the largest values obtained and so gives the maximum variations.

The reliability factors which we have attached to the final values are determined arbitrarily.

They are approximately twice the computed uncertainties as determined from the variations in the data and from the reliability with which individual constants in the apparatus could be determined.

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TABLE X. Dielectric constants of eight gases corrected to N.T.P.

Gas	Number of obser- vations	Tempera- ture limits (C°)	Value limits	Average value
Helium	11	24.65 24.75	1.0000674 693	1.0000684 ± 5
Neon	9	24.6 24.6	1267 1280	1274 ± 5
Argon	10	24.1 24.3	5440 5458	5451 ± 5
Hydrogen	10	25.25 25.3	2713 2733	2724 ± 10
Oxygen	9	23.85 24.4	5223 5241	5233 ± 10
Nitrogen	10	24.1 24.25	5789 5804	5796 ± 10
CO₂	11	23.85 23.9	9856 9899	9875 ± 20
Air (CO₂ free)	10	23.85 24.5	5654 5685	5669 ± 10

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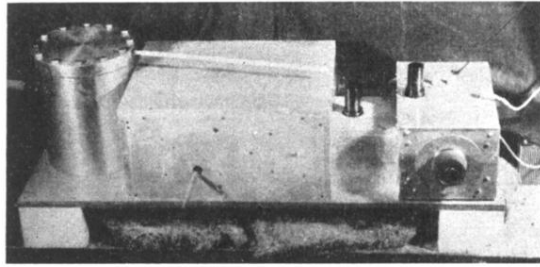(31) Van Vleck, Electric and Magnetic Susceptibilities, page 205.

Fig. 1