

Dielectric Constant of Water Vapor

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The frequently discussed deviations from linearity in the curves of $(K-1)/(K+2)$ versus pressure for water vapor have been investigated. It has been shown: (1) That with proper location of the insulators of the vapor condenser in weak fields, the dielectric constant curves for the vapor are linear until saturation is approached closely; they are linear over the entire range of pressures at which breaks have previously been reported; (2) that neither pronounced breaks similar to those reported by several workers, nor the small residual deviations always present near satura-

tion are due to the conductivity effect as commonly supposed; (3) that these breaks are due wholly to the added polarization contributed by the film of water molecules adsorbed on the insulator surfaces. Accurate dielectric data have been obtained for water vapor at 14 temperatures ranging from 21.3°C to 197.9°C; they can be represented by the equation $[(K-1)/(K+2)]RT/p' = (4.03 \pm 0.39) + (20,710 \pm 140)/T$. These data fall accurately along a Debye line, yielding an electric moment of $(1.831 \pm 0.006) \times 10^{-18}$ e.s.u. for the water molecule.

ON THE DEVIATIONS FROM LINEARITY

EARLY dielectric data for water vapor obtained by Jona¹ did not conform to the theoretical Debye line at the lower temperatures; the deviations were attributed to association of vapor molecules. Zahn² obtained data which showed the measured polarization of water vapor not at all proportional to the pressure at temperatures of 40°C or less. Pronounced breaks occurred at a pressure of the order of 1 cm of Hg; the lower the temperature the more pronounced was the break. Zahn attributed these breaks to the probable existence of a film of adsorbed water on the surfaces of the condenser plates. He pointed out that if observations were confined to pressures below those at which the breaks occurred, the data, while not accurate, were not inconsistent with the Debye theory. Wolf³ confirmed the general nature of the breaks reported by Zahn, but observed that they were entirely independent of plate spacing. He reported also that the magnitude of the break depended upon the insulating material used in the vapor condenser, being least for quartz; it appeared that even the slope of the line below the break was somewhat dependent upon the kind of insulator used. He further observed that the d.c. conductivity of the vapor condenser varied with the type of insulator used and with the pressure of the vapor in the condenser. The fact that the conductivity increased rapidly at approximately those pressures for which the breaks in the

dielectric curves occurred for the several insulators, led him to attribute the existence of the breaks to the conductivity effect. Zahn⁴ apparently confirmed these observations and was led to the same conclusion. Similar breaks, though occurring much nearer saturation, have since been observed for many materials. Maske⁵ reported them for benzophenone vapor; Knowles⁶ reported them for ethyl alcohol; and the author has found though not reported them for all vapors studied near saturation, including numerous alcohols, toluene and the nonpolar vapor benzene. Knowles studied variations in d.c. conductivity in the region of the breaks for ethyl alcohol vapor, and concluded that both experimentally and theoretically the breaks could not be caused by a conductivity effect; the conductivity effect was neither of the proper magnitude nor, for his experimental arrangement, in the proper direction.

Since there appears some evidence conflicting with each of the three suggested interpretations of the breaks (association, the added polarization due to adsorption on the condenser plates, and conductivity across the insulator surface), the author has undertaken to get at the real cause. He has chosen to study water vapor, that material yielding the most pronounced breaks. By use of an unusually stable heterodyne beat apparatus⁷ operating entirely on alternating current, along with a carefully calibrated variable

¹ Jona, *Physik. Zeits.* **20**, 14 (1919).

² Zahn, *Phys. Rev.* **27**, 329 (1926).

³ Wolf, *Ann. d. Physik* **83**, 884 (1927).

⁴ Zahn, *Phys. Rev.* **35**, 1047 (1930).

⁵ Maske, *Physik. Zeits.* **28**, 533 (1927).

⁶ Knowles, *J. Phys. Chem.* **36**, 2554 (1932).

⁷ Stranathan, *Rev. Sci. Inst.* **5**, 334 (1934).

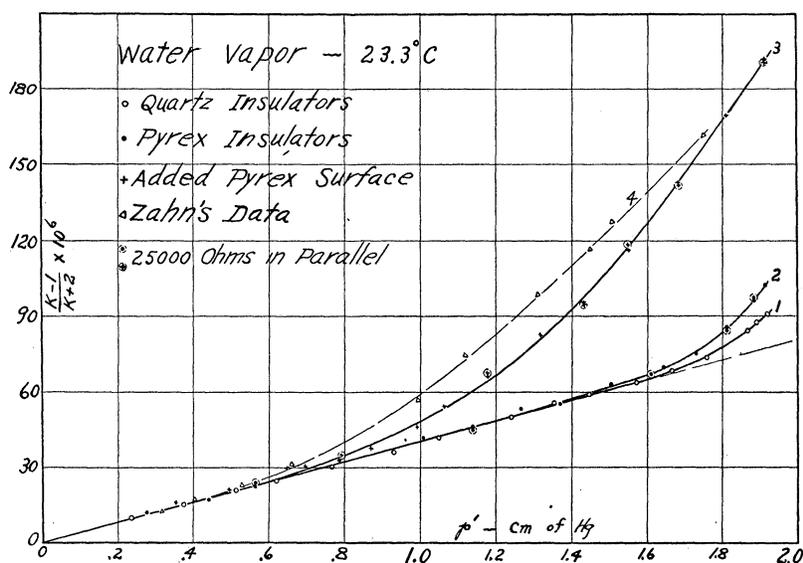


FIG. 1.

capacity standard,⁸ both previously described by the author, capacity changes as small as a few thousandths of a μf due to the vapor could be observed accurately. It was found⁹ immediately that by using a vapor condenser similar to that described by Knowles,⁶ in which care is taken to locate the insulators in weak fields, the dielectric polarization of water vapor varies linearly with pressure up to pressures far higher than those at which pronounced breaks have previously been reported. Large deviations could be observed only if the vapor were allowed to enter the condenser too rapidly; these could not be repeated and were probably due to local condensation. The addition of a tightly packed glass wool plug through which the vapor must pass in going from the vapor system (which was that used by Knowles⁶) to the condenser, completely eliminated any such possibility of error. Curve 1, Fig. 1 shows the results at 23.3°, using quartz insulators. Plotted in the same figure, curve 4, is the pronounced break reported by Zahn² for the same temperature, and confirmed approximately by Wolf.³ It is apparent that the present curve (1) is essentially linear up to the highest pressures for which observations were heretofore reported. Curve 2 represents data obtained using Pyrex

insulators. The break from linearity is somewhat larger and occurs at a somewhat lower pressure than for quartz, though it is even here not comparable with previously reported breaks. The slope of the line below the break is independent of the kind of insulator used. Fig. 2 shows similar data taken at 29.6°, curve 2 being the author's data obtained with Pyrex insulators, and curve 4 observations reported by Zahn. Even using Pyrex insulators, the curve is accurately linear up to pressures higher than the highest for which observations have been reported previously. While data using quartz insulators were not actually taken at this temperature, they have been taken for various nearby temperatures, and the results leave no doubt but that such a curve would be linear up to a still higher pressure, and the extent of the break less.

In spite of the fact that several observers who have measured the conductivity of the vapor condenser have attributed the nonlinearity of the dielectric curves to the conductivity effect, it has always appeared impossible to the author to reconcile the magnitude of the break with the measured conductivities. The author has therefore made three tests to show that the conductivity is not the cause of even the small residual breaks found here. First, since all previous workers seem to have measured d.c. conductivities, and since it is now recognized

⁸ Stranathan, Rev. Sci. Inst. 5, 315 (1934).

⁹ Reported at the Washington meeting of the Am. Phys. Soc., 1934.

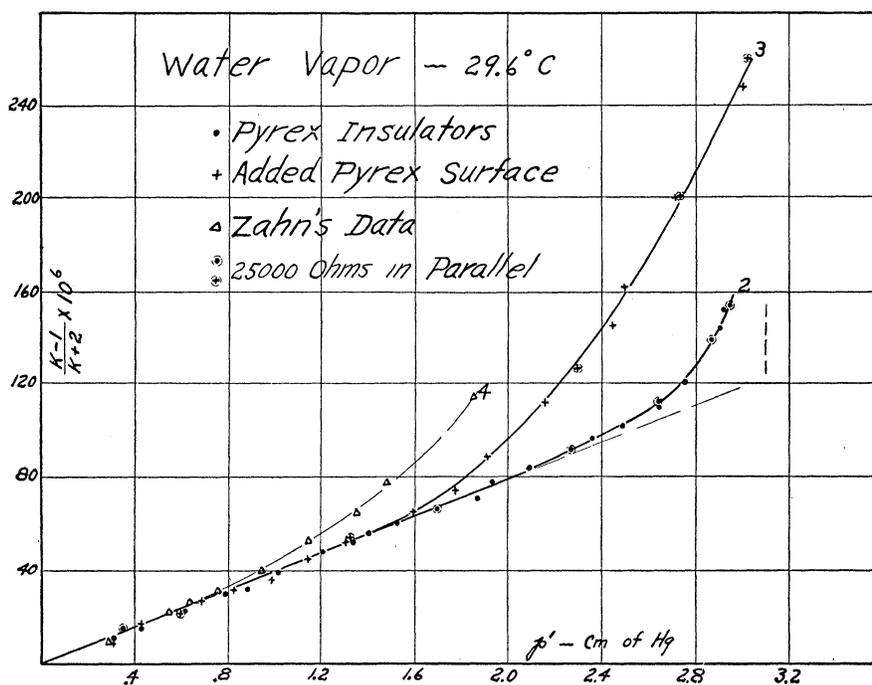


FIG. 2.

from the works of Yeager and Morgan¹⁰ and of Roberds¹¹ that the high frequency conductivity is larger than the d.c. conductivity, it seemed advisable to measure the conductivity of the vapor condenser at the same frequency as was used in making dielectric constant measurements. The author has made such measurements (at 545 kilocycles), by a method since described and used extensively by Roberds.¹¹ Since the large condenser (840 μmf) used in dielectric measurements is not conducive to accurate measurement of high leakage resistances at this frequency, no claim is made of accuracy other than as to order of magnitude. It can be stated definitely that the high frequency leakage resistance of the condenser was never less than 5 megohms at any vapor pressure of water less than saturation; except at pressures barely below saturation, it was very much higher. This value agrees with calculations from the specific conductivities quoted by Yeager and Morgan and by Roberds. Theoretically it appears that the magnitude of the break is entirely inconsistent with this high a leakage resistance.

¹⁰ Yeager and Morgan, *J. Phys. Chem.* 35, 2026 (1931).

¹¹ Roberds, *Physics* 6, 227 (1935).

Second, the author has made several experimental measurements of the effect of conductivity, measurements similar to those reported by Knowles.⁶ While it is impossible to introduce an artificial leakage resistance in parallel with the test condenser without introducing at the same time an appreciable capacity, it is possible by choice of appropriate resistors to introduce various leakage resistances all with essentially the same capacity; thence the effect of conductivity can be deduced. This has been done, using artificial leaks varying from 10^8 down to 10^4 ohms. Groups of such artificial leaks of several different types have been used, and the results obtained have been consistent as regards the magnitude of the conductivity effect. Experimentally the effect of conductivity is here in the proper direction but of entirely too small a magnitude to cause even the small residual breaks observed by the author. The leakage of the vapor condenser would apparently have to be at least 200 times as great as the actually measured value in order that the conductivity might produce breaks comparable with those observed.

Third, a test was made by placing an artificial leak directly in parallel with the vapor condenser

and leaving it there throughout the determination of the dielectric constant curve. Thus the vapor condenser was always of quite high leakage regardless of the pressure of the vapor within. It can easily be shown that, under such conditions, any change in leakage accompanying increases in vapor pressure would produce an entirely different effect upon the measured capacity than would be the case were the low resistance leak not permanently in parallel. As shown in both Figs. 1 and 2, dielectric observations, including the residual breaks near saturation, were identical with and without a permanent parallel leak of 25,000 ohms. Thus all three pieces of evidence here cited seem to show definitely that even the small residual breaks in the dielectric curves just below saturation cannot be caused by the conductivity effect.

In the test cited just above, one in effect changes the conductivity of the vapor condenser without changing the nature or extent of the insulator surfaces on which water molecules might be adsorbed. A test was next made under such conditions as would change markedly the extent of the adsorbing surface within the condenser without changing the leakage resistance. This was done in the following way: In the condenser used (see work of Knowles⁶ for diagram), the two sets of plates were built as two rigid metallic units. The one unit is then supported by four cylindrical compression insulators, 1.2 cm diameter, and 1.6 cm long. Three of these support the insulated unit on the bottom of the condenser housing, while the fourth is placed on top of the unit and has applied to it the compressional force which clamps the unit into place. While the normal plate spacing is approximately 1.5 mm, the insulators are all mounted between plates whose spacing is at least 10 times as large, thus placing them in a relatively weak field. Into the upper side of the lower of the two top plates (those between which the upper insulator was located) there were drilled 47 holes passing only part way through the plate. Into each of these was wedged in an upright position a piece of 8 mm Pyrex tubing carefully cut to such a length that it failed by approximately 2 mm to touch the adjacent plate. In this manner the effective insulator surface area which may adsorb water was increased by a factor

approximately 6 but, since the new insulator material touches only one plate, the leakage resistance of the condenser remains unchanged. Dielectric data¹² taken under these conditions are shown by curves 3 of Figs. 1 and 2. Again the same curve is obtained with or without the use of a permanent parallel leak of 25,000 ohms. The presence of additional adsorbing insulator surface thus emphasizes the break; the break is of much greater magnitude, the ratio of magnitudes being roughly the ratio of effective adsorbing surfaces, and it occurs in measurable magnitude at a lower pressure. Dielectric curves obtained under these conditions show breaks quite similar to those reported by Zahn and Wolf. One can scarcely escape the conclusion that all breaks obtained here are caused almost wholly by the added polarization contributed by the presence of a water film adsorbed on the surfaces of the insulators. While one cannot say definitely that previously reported breaks have not been due to conductivity, for it is always possible that an oscillator whose frequency is unusually dependent upon leakage has been used, still it appears unlikely indeed. It is far more probable that all such breaks have been caused by the added polarization contributed by the water film adsorbed on the insulators.

Two further experiments have been carried out to see whether the presence of such an adsorbed film of reasonable thickness would produce an added capacity of the proper magnitude to account for the observed break. An effort was first made to calculate, by rough approximation the capacity contributed by a film of given thickness, taking into account the fringing of the electric flux caused by the insulator and by the long thin adsorbed film of dielectric constant 80. Actual measurements of the capacity increases caused by similar though much thicker films (a few tenths of a mm thick) confined between two closely fitting pieces of glass tubing placed in a position between plates similar to that of the insulator, though touching only one of the plates, showed that the crude method of calculating the capacity contributed by the thin film gave surprisingly the right magnitude. Such experiments and calculations indicate that an adsorbed

¹² Reported at the Washington meeting of the Am. Phys. Soc., 1935. J. D. Stranathan, *Phys. Rev.* **47**, 794A (1935).

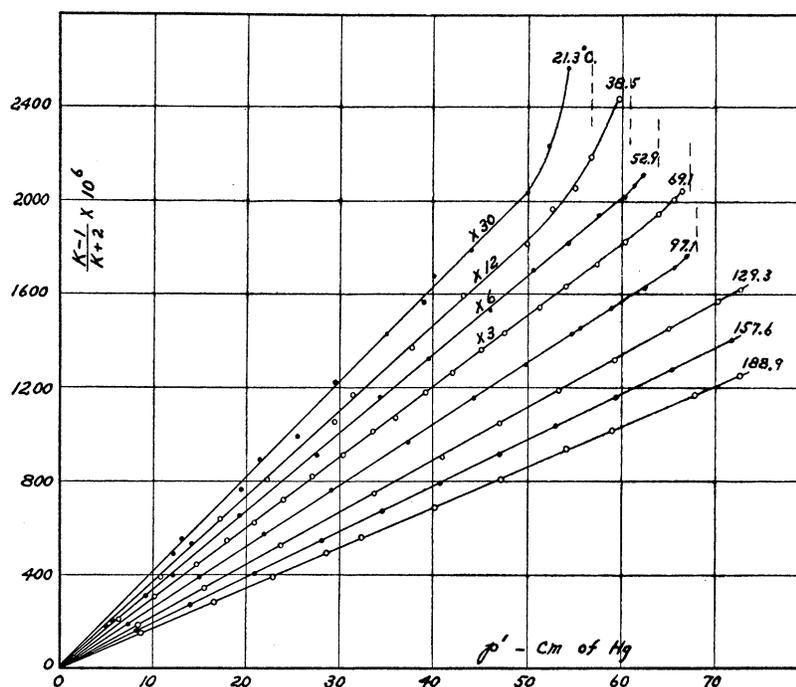


FIG. 3. For the lower temperature curves both ordinate and abscissa have been multiplied by the factor indicated.

water film a few hundred molecules thick would contribute a capacity increase sufficient to cause the deviation from linearity of the dielectric curve just below saturation. This requirement is quite consistent with the thickness of adsorbed films reported by various workers, McHaffie and Lehner¹³ for example, for glass near room temperature.

The second experiment was carried out with a "condenser" designed to emphasize any effect, either conductivity or capacity, of an adsorbed film. The actual piece used has been described by Roberds,¹¹ and consists of a series of conducting rings fitted tightly around a large Pyrex tube, alternate rings being connected together. The total capacity of this element, including that due to solid dielectric, was approximately 60 $\mu\mu\text{f}$. Calculations involving the number, length, and spacing of these rings show that for a given thickness of adsorbed film this element should show an increase in capacity 324 times the increase which would be caused by the same thickness of film on the Pyrex insulators of the

condenser used for dielectric measurements. Incidentally, it would also have 324 times the leakage. The increase in capacity of this element due to the presence of water vapor at 23.3°C was measured for a great number of pressures ranging up close to saturation. Measurements were made both with and without the permanent artificial leak of 25,000 previously referred to, and the results were entirely independent of its presence, indicating that even here the change in capacity observed was affected scarcely at all by any effect of conductivity. It is interesting that the resultant curve of capacity increase *versus* pressure of water vapor was quite similar to the curves obtained by plotting the number of molecular layers of water adsorbed *versus* the pressure from McHaffie and Lehner's¹³ data. As a specific example, the increase in capacity was 11.0 $\mu\mu\text{f}$ for a water vapor pressure of 1.8 cm of Hg. This increase may rightfully all be attributed to the film, for calculation shows that the vapor, with its observed dielectric constant, could account for less than 0.02 $\mu\mu\text{f}$ of the increase. If the capacity due to the film here is divided by 324, it appears that the same film present on the Pyrex

¹³ McHaffie and Lehner, J. Chem. Soc. London **127**, 1559 (1925).

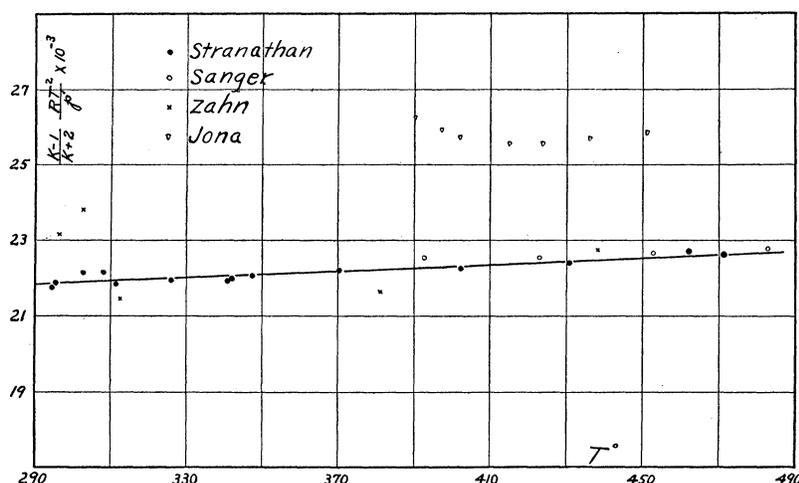


FIG. 4.

insulators of the condenser used for dielectric measurements should cause a capacity increase of $0.034 \mu\mu\text{f}$. The actual deviation from linearity of the dielectric curve at 23.3°C and 1.8 cm of Hg pressure, under which conditions this identical film exists, represents (from curve 2 of Fig. 1) a capacity increase of $0.030 \mu\mu\text{f}$. There can be no doubt that the added polarization due to the actual film of water adsorbed on the insulator surfaces will account quantitatively for the breaks observed in the dielectric curves for water vapor. The author suggests that probably all such breaks observed for various vapors are due mainly to this same effect. He has actually found that the addition of adsorbing insulator surface as mentioned above emphasizes the breaks for ethyl alcohol and for toluene, though no quantitative calculations have been attempted.

ON THE MOMENT OF THE WATER MOLECULE

Dielectric data have been taken at 14 different temperatures from 21.3° to 197.9°C , using quartz insulators. For the sake of clarity only half of these have been shown in Fig. 3. p' represents the pressure the vapor would exert were it an ideal gas; it is obtained from the observed pressure p and the van der Waals constants a and b , thus

$$p' = p \{ 1 + (p/RT)(a/RT - b) \}.$$

The molecular polarization is then given by

$$(K-1)M/(K+2)d = (K-1)RT/(K+2)p' \\ = A + B/T,$$

the last equality being a result of the Debye theory. The constant A should be equal to the molecular refraction at infinite wave-length, and B is related to the permanent electric moment μ of the molecule by

$$\mu = 1.272 \times 10^{-20} \sqrt{B}.$$

The molecular polarization at any temperature can be determined from the slope of the curve in Fig. 3. The best slopes of these lines were obtained by least squares, using all experimental points below the breaks.

Fig. 4 shows the product of molecular polarization and absolute temperature plotted against T . Previous data by Jona,¹ Zahn² and Sanger¹⁴ are indicated. The present data, including that at low temperatures, fall accurately on a straight line as demanded by theory; no point deviates by more than one percent. Sanger's data, though confined to the upper half of the temperature range here investigated, fall quite close to the present curve. Zahn's data, for which he makes no claim of accuracy, are not inconsistent with the present unless it be at the lower temperatures. A least-squares solution for the best straight line through the author's data gives

$$(K-1)RT/(K+2)p' = (4.03 \pm 0.39) \\ + (20,710 \pm 140)/T.$$

¹⁴ Sanger, *Physik. Zeits.* **31**, 306 (1930); *Helv. Phys. Acta.* **5**, 200 (1932).

The least-squares value for the electric moment of the water molecule is $(1.831 \pm 0.006) \times 10^{-18}$ e.s.u. The polarization 4.0 contributed by other than the permanent moment agrees within the probable error with the molecular refraction 3.7. In view of the range of temperature over which measurements were made, and in view of the fact that not one of the 14 points deviates by more than one percent from the Debye line, the moment here found should be quite reliable. Previously reported values have varied considerably. Jona¹ reported 1.87×10^{-18} , from early

vapor data. Stuart¹⁵ reported 1.79×10^{-18} . Williams¹⁶ obtained $(1.70 \pm 0.06) \times 10^{-18}$ by dissolving water in benzene. Sanger¹⁴ obtained $(1.842 \pm 0.008) \times 10^{-18}$ from vapor data. Sanger's value appears the most reliable of the group, though it was calculated using only three points all within a temperature range of 60°. Sanger's value and the present value, obtained from 14 points covering a temperature range of 177°, agree well within the sum of the probable errors.

¹⁵ Stuart, *Zeits. f. Physik* **51**, 490 (1928).

¹⁶ Williams, *Physik. Zeits.* **29**, 204 (1928).

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PHYSICAL REVIEW

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The Rate of Change of Electron Temperature in the Mercury Afterglow

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A study has been made of the behavior of a plasma in which no new ions are found, as regards electron temperature and concentration, to determine the sources of the electron energy. Measurements were made with a movable probe in a stream of ionized mercury vapor passing out from an arc discharge. The velocity and vapor concentration were determined by stroboscopic measurements on moving striations produced by an impressed alternating voltage. The vapor concentration, expressed in pressure reduced to 0°C, varied between 0.05 and 1.5 mm of mer-

cury. The rate of cooling of the electrons was very rapid at first, but below 2500°K this rate decreased rapidly. Finally the electron temperature reached a constant value which was several hundred degrees above that of the vapor, the difference being proportional to the vapor concentration. The most reasonable source of energy necessary to keep up the electron temperature seems to be either the local recombination process, directly or through the metastable atoms formed, or the metastable atoms brought down the tube by the vapor stream.

INTRODUCTION

INVESTIGATIONS of the velocity distribution of free electrons in the plasma of an arc discharge¹ and in the plasma which diffuses out of the direct discharge as the afterglow, show that the Maxwellian law is followed, so that the distribution may be stated in terms of temperature. The conditions in the afterglow have been studied by a number of investigators² and the rate of recombination has been found to be

closely connected with the electron temperature. The variation of the electron temperature in the afterglow indicated that the electron energy was markedly affected by the various conditions in a plasma in which there was present no new excitation or ionization. The purpose of the present investigation was to study the important factors in more detail by observing under varying conditions the time-rate of decrease of the electron temperature and concentration in the afterglow.

¹ I. Langmuir and H. M. Mott-Smith, *Gen. Elect. Rev.* **27**, 449, 538, 616, 762, 810 (1924); I. Langmuir, *Phys. Rev.* **26**, 585 (1925); H. M. Mott-Smith and I. Langmuir, *Phys. Rev.* **28**, 727 (1926); T. I. Killian, *Phys. Rev.* **35**, 1238 (1930); R. Seeliger and R. Hirschert, *Ann. d. Physik* **11**, 7, 817 (1931).

² F. L. Mohler, *Phys. Rev.* **31**, 187 (1928); Mohler and Boeckner, *Bur. Standards J. Research* **2**, 489; **3**, 303 (1929); H. W. Webb and S. C. Wang, *Phys. Rev.* **33**, 329 (1929); H. W. Webb and D. Sinclair, *Phys. Rev.* **37**, 182 (1931).

EXPERIMENTAL

The discharge tube used is shown in Fig. 1. Between the hot cathode³ *C* and the anode *Q*

³ For this we are indebted to the General Electric Vapor Lamp Co.