THE MAGNETIC SUSCEPTIBILITY OF GASES.' II.

By W. P. Roop.

8. The method of the gas manometer, as it may be called, has now been applied to the determination of the susceptibility of oxygen. Three features of the new determination distinguish it from previous work in the same field: observational errors have been reduced to values hitherto unattained; the observations have been made in fields of small intensity; and certain systematic errors of methods previously used have been eliminated.

Precision of measurements in this field has been very little discussed for the reason that previous work has shown wide discrepancies between successive observations taken by a given investigator, as well as between the averages obtained by different investigators. In Section 9 will be found a discussion of the work of Piccard,² the only previous observer who claims for his data a moderate degree of exactness.

The intensity of the field used is of importance for two reasons. In the first place, the measurement of a field of high intensity, but small extension, is a matter of considerable difficulty, and subject to undoubted errors for which allowance can not be made. In the second place, measurement of susceptibility in fields of both high and low intensity is necessary in order to obtain an experimental answer to the question: is suspectibility entirely independent of field intensity? This question will receive further consideration in Section ro.

Three systematic errors of other methods are absent in that of the gas manometer, namely: error due to the uncertainty as to the susceptibility of water; error due to imperfect determinations of pressure in the gas; and error due to solution of the gas in the liquid of the liquid manometer. These matters are discussed in detail in Section I3. In addition, the high sensitivity of the method reduces observational errors as well, since one source of the large errors of previous work has been the smallness of the quantities measured.

9. Piccard's paper unfortunately does not exhibit the data from which his mean values are calculated. It would appear, from data given on page 462 of his paper, that the probable error of an average of r5 deter-

¹ A continuation of work described in PHYSICAL REVIEW, 2, 497, 1913.

^{&#}x27; Piccard, Archives des Sciences, 3g, 476, I9I3.

minations of the magnetic depression of water (Ouincke's method) is 0.0028 mm. Since his determination of the susceptibility of oxygen is based on two such observations, it would seem to be subject to errors of that order of magnitude, or larger. On his page 479, the observed difference in magnetic depression of water due to presence of oxygen atmosphere is 0.033 cm. (misprinted in one place as mm.). The observational error in his mean result thus appears to lie between one and two per cent.

Observational error occurring in the use of the gas manometer is well under one per cent.

10. Systematic variation of susceptibility with field intensity has been observed by both Quincke¹ and Hennig.² A summary of data taken from their papers, and reproduced in the following table, shows this. The units in which susceptibility is expressed here and elsewhere in this paper, are ten millionths (10^{-7}) .

| Quincke. | | Hennig. | | | | | | |
|----------|----------------------|---------|------|---|-------------------------------|--|--|--|
| | $\kappa \times 10^7$ | H | | κ X ¹⁰⁷ I Atmos. κ X ¹⁰⁷ 2 Atmos. | $\kappa \times 10^7$ 4 Atmos. | | | |
| 7,000 | 1.52 | 3.700 | 1.31 | | 1.15 | | | |
| 14,000 | 1.57 | 5.700 | 1.26 | | 1.26 | | | |
| 16,000 | 1.70 | 8.400 | 1.26 | 1.23 | | | | |
| | | 10.340 | - 10 | -15 | റ | | | |

TABLE I. Data on Variation of κ with H.

Both men, however, evidently considered their data insufficient to warrant even the suggestion that such a variation exists, for neither mentions the matter. The fact that the variation is in the opposite sense in the two cases is evidence of its spurious character. On account of the care used by Hennig, however, this should not have deterred him from calling attention to the indication given by his data. Instead of that, he excluded the two extreme values in casting up his definitive average.

Curie simply states, without giving data, that the susceptibility of oxygen was found not to vary within the limits of 100 and 1,350 gausses. These are much weaker fields, however, than those used by Quincke and Hennig, and his mean value is high, namely: 1.67. This was based on an assumed value for water of 7.9. The recent carefully determined value reached independently by Piccard and Sève is 7.2. This would convert Curie's value to 1.52.

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¹ Ouincke, Annalen der Physik, 34, 401, 1888.

² Hennig, Annalen der Physik, 50, 485, 1893.

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Piccard's value of 1.407 was obtained with a more intense field $(21,000)$ gausses) than that used by any of the others.

Langevin's theory of magnetization of gases demands a decrease of susceptibility with increasing field intensity, but according to his estimate, this should only begin to be perceptible at fields of the order of Ioo,ooo gausses at atmospheric temperatures. The systematic variation shown by Hennig's data, and the discrepancy between the results of Curie and of Piccard would indicate that the field intensity at which saturation begins to be appreciable is not so high as that. A comparison of Piccard's work with the new results exhibited at the end of this paper may be considered to point to the same conclusion.

II. The apparatus used in the present experiments is the same in principle as that previously described, but quite different in design. It seemed impracticable to obtain a manometer of the desired form in glass. In order to reduce the time required for the enclosed gases to settle to their equilibrium position, it was necessary to make the bore of the manometer large and uniform. It also seemed desirable that it should be circular in shape, and that the two valves should be opened and closed simultaneously. The only feasible way of doing this was by using metal as a material. Since iron was excluded for magnetic reasons, mercury could not be used for handling the gas. It was therefore determined to make use of a vacuum pump and exhaust the manometer completely at each trial. The exhaustion demanded is about 0.01 mm., and difficulties were encountered in making the somewhat complicated brass manometer tight. This, however, was finally accomplished, and the present limitation to precision lies mainly in temperature control.

The manometer consists of a brass block containing a toroidal cavity of mean radius 46.7 mm., and cross-sectional area 33.33 mm.² At opposite ends of a diameter, the toroid is divided by two ground stopcocks, connected by gear wheels so as to turn together. The diameter along which the toroid is thus divided is inclined at an angle of 2o' with the horizontal.

Each chamber of the manometer may be connected separately with the vacuum pump, which is of the Toepler type. By means of this pump, the gas may be transferred to the burette, and its volume measured. On the way to the pump, the gas passes through a drying tube and an absorption tube filled with solid KOH.

The figure indicates schematically the arrangement of the apparatus.

Iz. The operations leading to a value for susceptibility may be summarized as follows: First, the cocks A and B , leading to the two chambers of the manometer, were opened, and the entire apparatus exhausted.

Cock C was turned so as to pass the gas into the atmosphere. At the same time the burette was completely filled with mercury by raising reservoir F until mercury flowed through cock C (now in its other position) into the chamber G . On reversing C again and raising reservoir E , all air was expelled from G . C was then closed and left closed. Cocks A

and B were now connected, respectively, with a supply of oxygen and of carbon dioxide. On opening the cocks A and B, the upper chamber of the manometer was thus filled with oxygen and the lower chamber with carbon dioxide. Now on closing A and B and opening the brass cocks of the manometer momentarily, the gases Howed around until the two boundaries between them lay at opposite ends of a horizontal diameter. Diffusion, of course, occurred at the same time. Difficulties thus introduced have already been treated in sections 4 and 5, and will be again discussed in section 17. After the manometer cocks were closed again, the upper chamber had received a small amount of carbon dioxide, and the lower chamber an equal amount of oxygen. Passing the gas into the burette, measurements of the volume of oxygen in each chamber were obtained.

The whole process was then repeated, with the exception that the two chambers of the manometer were connected with each other under the inHuence of the magnetic field. The boundaries between the two gases thus reached different equilibrium positions, and the volumes measured in the burette were different from those obtained before.

If the action of the field is to decrease the volume of oxygen left in the upper chamber, the volume of oxygen found in the lower chamber will be increased. This increase and decrease should be numerically equal, and in this way we obtain a valuable check on all observations.

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We will call this observed deviation in volume ΔV . Divided by the cross-sectional area of the toroid, it gives the vertical displacement of the boundary surface due to the action of the field. This we will call l instead of d, as in Section 3.

The intensity of the magnetic field was determined by means described in Section 23.

The susceptibility difference between oxygen and carbon dioxide is given by the equation

$$
\kappa-\kappa_0=\frac{4lg(\rho-\rho_0)}{H^2-H_0^2}.
$$

I3. Before proceeding to the discussion of the experimental details, I wi11 call attention to certain broad features of the method.

In the first place, it is a comparison only, and not absolute in character. The same is true of all other methods that have ever been applied to the problem. In the cases of Quincke, Curie, and Piccard, the comparison substance was water, with respect to whose susceptibility an uncertainty of absolute value o.5 exists, unless the work of Piccard and of Seve be accepted and all previous work rejected. In Quincke's method, used also by Piccard, error of the same absolute amount must be considered to attach to the value for oxygen, since it is the difference of susceptibility of oxygen and water that is measured. On the other hand, this uncertainty is reduced in case the oxygen is used under pressure greater than that of the atmosphere. Piccard does not state the pressure used, but only indicates that allowance for pressure was made in reducing data. Curie's method introduces uncertainty, not of the same absolute magnitude as that in the case of water, but in the same proportion. Hennig's method compares susceptibilities of oxygen and air, and is based on the assumption that the susceptibility of air is due simply to its oxygen content.

The adoption of carbon dioxide as comparison susbtance leads to uncertainty of the same order of magnitude as that which exists with respect to the susceptibility of that gas. I have given elsewhere' a summary of work on carbon dioxide which indicates that its susceptibility is certainly less than o.o3. Since different observers disagree, even as to sign, we may, in default of better knowledge, take its value to be zero. The uncertainty thus introduced does not exceed 2 per cent. of the susceptibility for oxygen.

I hope to completely settle this difficulty by the application of an absolute method now in hand.

¹ Physikalische Zeitschrift, 12, 55, 1911.

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Another feature of the method of the gas manometer is that its indications are not affected by variations in pressure, except to the relatively small extent that specific susceptibility (susceptibility divided by density) depends on the state of compression. On the other hand, in Quincke's method, observed manometric depressions are in direct proportion to the pressure. This independence of pressure makes the method valuable for two reasons: no pressure correction is necessary; and the method is available for determining the variation of specific susceptibility with pressure, without diminution of precision at low pressures.

On the other hand, the method is rather sensitive to temperature changes, necessitating exact thermostatic control in an attempt to better the results here presented.

One type of difficulty inherent in Quincke's liquid manometer is completely avoided in the gas manometer, and that is the uncertainty as to the effect of solution of gas in the liquid. Even Piccard introduces no correction on this account, although an observation which he makes in another connection' would indicate that it is of considerable importance. From this difficulty Curie's work is exempt.

x4. I will now proceed to discuss the following essential matters of detail in the present experiments: (a) Purity of gases; (b) Precautions in filling and operating manometer; (c) Diffusion in the manometer; (d) Temperature control; (e) Determination of sectional area of manometer; (f) Correction for curvature of manometer bore; (g) Field intensity measurements.

t5. The gases were of the kind used for commercial purposes, stored in steel cylinders. The carbon dioxide was analyzed by absorption in the apparatus itself. In a number of trials, the largest volume of gas unabsorbed by solid KOH was observed to be 10 mm.³ out of a total of 5,300 mm.³ This quantity of air (the chief impurity) could neither cause an appreciable deviation from the density of pure carbon dioxide, nor affect the magnetic forces by its oxygen content. Therefore no correction was made for it.

The oxygen was obtained from the Linde Air Products Co., and was stated to contain about 2 per cent. of nitrogen. This figure was checked by a simple analysis. A glass bulb of 200 c.c. capacity was fitted with a stopcock at each end. It was filled with oxygen by running a steady slow stream of gas from the cylinder through it for five to ten minutes. While the gas was still running through, the lower end of the open tube was placed under the surface of a strong solution of KOH, and the upper cock was closed. The gas in the bulb was warmed with the hand, and a few

 1 Piccard, loc. cit., p. 481 .

bubbles driven out. When the temperature returned to that of the room, the KOH solution stood at an observed point in the bottom of the bulb. Pyrogallic acid was then poured in from above in such a way as to admit no air, at first only in small quantities. As absorption proceeded, the solution rose in the bulb, and more and more pyrogallic acid was added, until absorption was complete. The bulb was calibrated by water weighings. Two determinations yielded values of 98.03 and 97.84 for the percentage of oxygen in the gas. The mean was taken as the correct value. This somewhat crude, but very convenient analysis amply satisfies all demands of precision for the purpose in view.

x6. The How of gas from the cylinders was controlled by reducing valves, and the gas was admitted to the manometer through rubber tubes. Before each run, the rubber tube was detached from the cock and a slow steady stream directed against the opening in the end of the glass tube for two to ten minutes, depending on how recently the operation had been carried out before. The tube projecting from the cock was about I cm. long, and of capillary bore. It would appear that pure gas from the cylinder would thus reach the manometer, although failure to meet this condition may be partly responsible for the residual lack of uniformity in the observations.

Both gases were dried, and the oxygen was passed through KOH to insure the absence of carbon dioxide.

As soon as the rubber tube was placed over the end of the glass tube, the How necessarily stopped, and the reducing valve maintained in the tube a steady, but small pressure. The cock (A, B) leading into the manometer was then opened, momentarily reducing the pressure, but not permanently. The reducing valve was then closed and a side cock opened for an instant to reduce the pressure in the tubes and chamber to that of the atmosphere. This, of course, was accompanied by a slight cooling of the gas in the manometer. After an allowance of time (three minutes) for the gas in the manometer to recover the temperature of the brass walls, the side cock was again opened momentarily, and the cock (A, B) leading to the manometer was then finally closed.

In spite of these elaborate precautions, the outstanding non-uniformity in observations seems to be largely due to failure to control the temperature, and hence pressure of the gas inside the manometer.

I7. After the manometer had been filled, the brass cocks were opened for a certain length of time to allow the gases to settle into their equilibrium position. This time must be long enough not to interrupt the motion before the equilibrium position has been reached, and short enough to prevent diffusion beyond the limits of the uniform field while the cock still remained open.

To explain the means by which these conditions were satisfied, I will refer to the detailed drawing of the manometer. The broken circles

represent the toroidal bore; M and N are the two cocks, with diagonal bore, as indicated.

The bore of the manometer is large (diameter, 6 mm.) so as to reduce the viscous resistance to the metion of the gases. In order to reduce to a minimum the inevitable mixing during motion of the boundary, the distance through which the boundary must move is Fig. 2. made as small as possible.

The time during which cocks \overline{M}

and X were left open was determined in accordance with indications as to diffusion obtained in the following way: a series of runs was carried through, with zero magnetic field, and with the cocks open for a length of time varying from I to 5 seconds. The results as exhibited in the table show that I second is certainly too little time, while 5 seconds is

TABLE II. Table to Illustrate Diffusion.

| $Time, Secs. \ldots \ldots \ldots$ | | | | | | | | | |
|------------------------------------|--|-----|-------|---------|-----|--|--|--|--|
| Burette reading, mm^3 464 | | 532 | - 535 | - 520 - | 532 | | | | |

certainly too much, since in that time an appreciable amount of oxygen has *diffused* into the lower chamber. The four observations running from 1.6 to ^g seconds, however, show no discrepancies exceeding the observational errors. As a result of this test, 2.^g seconds was taken as the standard length of time during which the cocks were held open. Exact determination of this time being unnecessary, opening and closing was done by hand, and time estimated to fifths of seconds by ear.

The question was also investigated, with similar results, with magnetic field on as well as off.

I.8. Certain details of design of the maonmeter were found essential to its proper operation.

Difficulty connected with the disposal of the gas contained within the rather large bore of the cock was settled as follows: a groove was cut around the plug in such a way as to intersect one of the open ends of the

bore of the plug. In this way, one of the plugs was connected with one chamber and the other with the other, in whatever position the plugs stood. The division of the gas in the manometer into two halves was thus sharp and without any ambiguity of any kind. The design of the plug is illustrated by the accompanying photograph.

In constructing the manometer, it was necessary to turn the cavity out in two plates which were then put together, face to face. The second photograph shows a section of the manometer. The large circle in the center is the section of the cavity, and the horizontal lines extending to each side are the sections of the faces of the plates. It was found

Fig. 4.

impossible in this way to make a permanently tight joint by simply soldering the two plates together, and recourse was had to an expedient which settled the difficulty satisfactorily. Just inside and outside the cavity, shallow grooves were cut in the faces of the two plates, and the sections of these may also be seen in the photograph. After the plates were soldered together, these grooves were squirted full of sealing wax. In order that the seats of the cocks might not be subject to the action of the exposed section of this sealing wax guard ring, they were somewhat enlarged and a bushing inserted. The cock plugs, which were of phosphor bronze, thus were ground into a uniform jointless brass surface, with satisfactory results.

I9. The temperature of the brass manometer was closely observed by means of two thermometers, graduated to twentieths of a degree, whose bulbs were placed in cavities in the brass. The two thermometers rarely agreed exactly. The burette was water jacketed to retard temperature changes. Corrections for temperature difference between manometer and burette amounted, in the maximum, to 10 per cent.; in the average, to 2 per cent. Sufficient precautions were taken, however, to reduce uncorrected errors from this source well below I per cent.

Different runs were effected at different temperatures ranging from 13° to 20° C. No attempt was made to correct individual runs according to Curie's law, so that deviations from the average due to this cause are included with observational errors.

2o. The bore of the manometer was determined by sawing a right section of it, and enlarging photographically. The area of the photograph (See Fig. 4) was determined by means of a planimeter. The scale shown in Fig. 4 is a scale of millimeters ruled on the brass surface with a dividing engine.

21. If the manometer were of uniform, vertical bore, l , the vertical deviation of the boundary due to the action of the field, would be simply ΔV , divided by the area of cross-section. Since the bore is circular, instead of straight and vertical, we must introduce a correction. Let a_0 denote the area of the normal section, and α that of the approximate horizontal section at the point at which the boundary rests in the deviated position. Referring to the figure, we see that

$$
l = r_1 \sin \theta = r_1 \sin \frac{\Delta V}{a_0 r_1}.
$$
 (3)

This is based on the assumption that the boundary remains horizontal, and that equation (I) is exact. The latter condition is not satisfied, and we proceed to determine the error as follows: The true value of the horizontal sectional area we will denote by $a(I + \epsilon)$. ϵ will, of course, vary with l, but by obtaining a number of distributed values, and taking the average, we can determine a factor which can be taken out from under the integral and applied directly to the approximate result. To do this, we determine the exact area of horizontal cross-section as a function of l , r_1 and r_2 .

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Measuring x horizontally in the plane of the toroid, y vertically, and s normally to the plane of the toroid, we have, as the equation of the toroidal surface,

$$
z^{2} + (\sqrt{x^{2} + y^{2}} - r_{1})^{2} = r_{2}^{2}.
$$

The equation of the line of intersection with the plane

1s

$$
z = \sqrt{r_2^2 - (\sqrt{x^2 + l^2} - r_1)^2},
$$

 $z = \pm l$

and this is the curve bounding our horizontal section. To determine its area, we must evaluate the integral

$$
\int_{r_1-r_2}^{r_1+r_2} z dx.
$$

This I have not been able to do in general, but numerical evaluation at a series of values of l is simple and yields the desired result with sufficient exactness.

I find the maximum error to be 4.0 per cent., and the mean error, $\bar{\epsilon}$, 2.0 per cent., in the case where the correction is largest

The corrected value of l is obtained from the equation

$$
l = r_1 \sin \frac{\Delta V(\mathbf{I} - \bar{\epsilon})}{a_0 r_1}.
$$
 (4)

22. ln entire agreement with Piccard, I find that more careful attention is necessary in measuring the intensity of the field than has been given it in the past. A search coil and ballistic galvanometer were employed for the purpose. The coil was made by the builders of the magnet, the Société Genevoise, but the data accompanying the coil were found not to be trustworthy. The coil was calibrated by comparison with two precision coils, wound on glass. These two coils were constructed with great care and checked against each other to insure accuracy. Glass cylinders 20 \times 6 mm. were ground true and calipered. Glass discs were cemented to their sides, and on each of the spools thus formed, a single layer, consisting of 25 turns of s.s.c. No. 34 copper was wound. The ends were specially arranged to avoid introduction of unevaluated magnetic area. The two coils were found by comparison in a field of 2,ooo units to show a discrepancy of less than o.2 per cent. The value of the area of the Geneva search coil as determined by comparison with the glass coils, may safely be stated to be in error by an amount not exceeding a similar figure.

Dependence was placed on the calculated area of the glass coils.

Experiment showed this to be far more satisfactory than any scheme of calibration of the coils in a calculated field.

The galvanometer was not in any sense used as a measuring instrument. It was calibrated carefully in connection with each reading with the search coils, at the identical deflections observed with the search coils. A standard solenoid and calibrated ammeter were used for the purpose.

2g. I will now proceed to consider the data obtained. I give first in full the record of a sample pair of runs.

2g. In all, x4o runs like these were carried through. Of these, a great many, most of the first and second series, were rejected. Of the third series of 65 runs, a few also were rejected. No run was rejected by reason of its deviation in value for ΔV from other runs. The sole criterion was agreement as to total volume of unabsorbed gas.

There was a considerable unexplained variation in the value of this total volume of unabsorbed gas, but changes did not often occur suddenly. For this reason, readings at zero field were taken frequently, and com-

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bination of successive runs in pairs like that shown above gives consistent results. When sudden variations did occur, they were taken as evidence of leakage, or failure to absorb perfectly, and the readings rejected. Attempts were made to correct on a basis of equalization of total volume of unabsorbed gas. The probable error was found to be somewhat reduced in this way, but the mean values did not change appreciably. Results as given are uncorrected.

25. Data from which the average ΔV for $I = 5.00$ amps. was obtained were as follows:

1,543 1,507 1,579 1,527 1,607 1,631 1,504 1,551 1,593 1,594 1,571 1,581 1,527 1,507 1,527 1,528 1,572 1,614 Mean value, $\overline{1,559} \pm 10$.

The averages at different field intensities are given in the table.

26. Applying all corrections as indicated, I find

at $H = 7{,}495$, $\kappa = 1.459 \times 10^{-7}$, at $H = 3,405$, $\kappa = 1.459 \times 10^{-7}$;

less trustworthy are the other two determinations:

at
$$
H = 1,833
$$
, $\kappa = 1.41 \times 10^{-7}$,
at $H = 1,080$, $\kappa = 1.6 \times 10^{-7}$.

The agreement between the first two figures is partly coincidental. I

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judge, however, that it is fair to state that the true value differs by less than 0.01 \times 10⁻⁷ from 1.46 \times 10⁻⁷.

27. The discrepancy between this result and that of Piccard exceeds the estimates of probable error. This might be explained in four different ways. (a) The error may be larger than it is estimated to be. Experience shows that this is sometimes the case in work involving a number of possibilities of error. (b) The susceptibility of carbon dioxide may differ from zero. (c) Piccard's result may be in error by reason of failure to correct for dissolved oxygen, or by reason of error in the value for susceptibility of water. (d) Oxygen may show saturation phenomena at field intensities lower than Langevin's estimated limit.

The following table may be taken to give the best answer available at the present time to the question of magnetic saturation in oxygen.

Further experiments in continuation of these here described are in progress. Acknowledgment is due the Whiting Fund, from which the magnet was purchased, Mr. W. R. Stamper, who constructed the manometer, and Mr. O. G. Steinitz, who constructed the standard search coils.

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Fig. 3.

Fig. 4.