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Diamagnetism of Water at Different Temperatures

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Attention is called to the discordant results found by different observers for the diamagnetism of water at different temperatures. A new and very sensitive device called a manometric balance is described. The device was designed for the purpose of investigating the variation of the specific susceptibility of water with varying temperature. Experiments with water which had just been boiled in order to get rid of dissolved air indicated less diamagnetism at temperatures higher than 23.5°C; and experiments upon water which was boiled and left standing for several days in contact with helium gas indicated greater diamagnetism at temperatures higher than 23.5°C; the change in the specific susceptiblity was less than one percent in each case.

THE subject of the present communication has already received considerable attention from various experimentalists. The results obtained by different investigators,[1] using different methods, are not in agreement; in fact, the variations found for the specific susceptibility of water do not always agree as regards sign; for example, Piccard, using a modified Quincke method, found that the diamagnetism of water is greater at higher temperatures, while Cabrera and Duperier, using a torsion method, found it to be less. The magnitudes of the variations found were in all cases less than 3 percent of the specific susceptibility (susceptibility per unit mass) of water at 20°C, which from previous absolute measurements is known to have a numerical value of -0.72×10^{-6}, approximately, in c.g.s. units.

At a recent meeting[2] of the French Academy a summary of the results obtained by the various investigators referred to above was presented in the form of a diagram. This diagram on a somewhat different scale is reproduced in Fig. 1, a curve representing the results of Mathur, obtained in 1931, being added. The lack of agreement in the results obtained by these investigators for the diamagnetism of water at different temperatures is very remarkable, and the reasons therefore seem very obscure.

The purpose of the present paper is to describe a new method for the investigation of the phenomena in question, and to present the results of some preliminary experiments which may serve to throw some light upon the anomalous results previously obtained.

The device which we employ is called a manometric balance and operates on the principle of balancing the actions of two magnetic fields, one acting upon water at some specified temperature and the other upon water at a

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[1] Du Bois, Wied. Ann. **95**, 167 (1888); Jager and Meyer, Wied. Ann. **67**, 427, 707 (1899); Piaggesi, Phys. Zeits. **4**, 347 (1905); Piccard, C. R. **155**, 1497 (1912); Marke, Bull. Acad. Danemark p. 395 (1916); Cabrera and Duperier, Jour. d. Physique et le Radium **6**, 121 (1925); Mathur, Ind. Jour. Phys. **15**, part 3, 207 (1931).

[2] See Comptes Rendus **191**, 589 (1930).

standard temperature. The theory of the balance will be given after the apparatus itself has been described.

THE MANOMETRIC BALANCE

In Fig. 2 the letter M designates one of the two coaxial cores of an electromagnet, each core being about 10 cm in diameter, and M_1, M_2 designate two of four equal pole-tips in the forms of truncated cones, cemented on M; the smaller circular faces of these pole-tips were about 1.5 cm in diameter. The second core M' (not shown in the figure) is also provided with two pole tips M_1', M_2' (not shown in the figure) facing M_1, M_2; the gaps between M_1, M_1' and M_2, M_2' were approximately 1 cm in length.

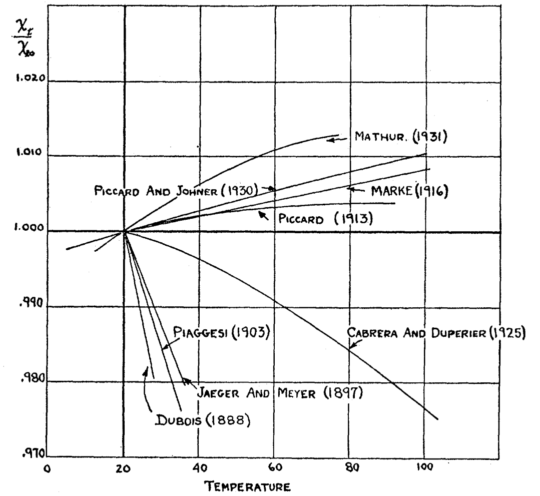

Fig. 1. Summary of results obtained for χ_t/χ_{20}.

The manometric balance itself is made of Pyrex glass throughout, and consists of two branches, a left branch and a right branch. Its essential features are represented in Fig. 2 with designations whose significance is given in the legend below the figure.

The procedure of filling and adjusting the balance is as follows. After mercury has been introduced to the same level in the bulbs E_1, E_2, the stopcock connecting these bulbs is closed, and liquids are then admitted to the two branches through the filling-funnels A_1, A_2. After the liquids have reached the tubes t_1, t_2 at the bottom, the 3-way stopcocks B_1, B_2 are so set as to connect each branch with a corresponding mercury cup which, by a vertical adjusting screw C_1, or C_2, can be raised or lowered so as to bring the corresponding meniscus m_1, or m_2, to approximately the desired position in the meniscus tube t_1, or t_2, between the pole-tips M_1, M_1', or M_2, M_2'. The stopcocks B_1, B_2 are then closed and further adjustments of the menisci m_1, m_2 are made by varying the currents through the resistance coils designated in the figure as coil 1 and coil 2, whereby expansion or contraction of the portions of the liquid columns which they enclose is produced.

The liquid used in the right branch was water at the standard temperature T_0, (23.5°C), and in the left branch water at some temperature T, or a calibrating solution of nickel chloride at the standard temperature.

The positions of the menisci with respect to their respective pole-tips are determined by two telescopes (not shown in the figure) provided with micrometer eyepieces.

The right branch of the balance is connected with a funnel F through which water containing suspended particles of anise oil can be admitted when desired, the motion of which in the capillary tube designated *Cap* could be observed through the microscope designated *Mic*. The device designated *Cell* through which the capillary tube passes is essentially a tube of brass provided with glass ends and filled with Canada balsam.

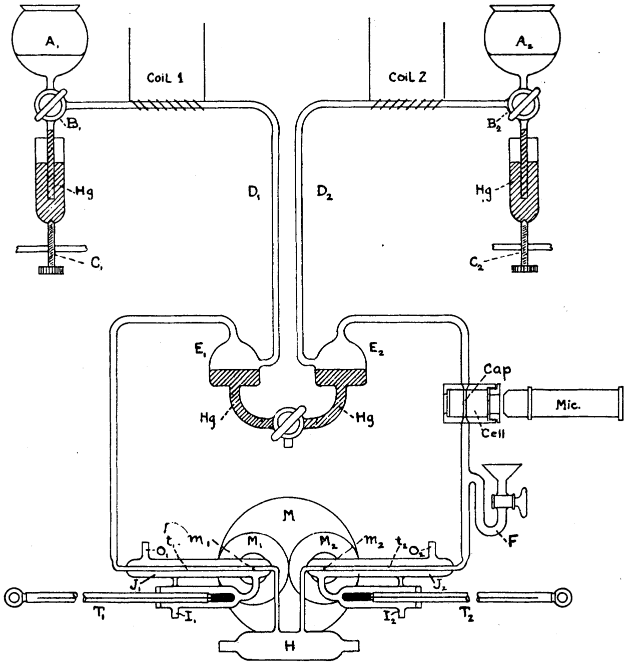

Fig. 2. Manometric balance.

A_1, A_2	—Filling funnels
B_1, B_2	—3-way stopcocks
C_1, C_2	—Adjusting screws
Cap	—Capillary tube
Cell	—Canada balsam container
Coil 1	—Resistance coil
Coil 2	—Resistance coil
D_1, D_2	—Auxiliary tubes
E_1, E_2	—Equilibration bulbs
F	—Inlet funnel
H	—Helium container
Hg	—Mercury
I_1, I_2	—Inlets for water jackets
J_1, J_2	—Water jackets
M	—Core of electromagnet
M_1, M_2	—Pole tips of electromagnet
m_1, m_2	—Menisci of liquids
O_1, O_2	—Outlets for water jackets
t_1, t_2	—Menisci tubes
T_1, T_2	—Thermometers

The letter J_1 designates a jacket enclosing the meniscus tube t_1, provided with an inlet tube I_1 and an outlet tube O_1, through which liquid at any desired temperature can be passed for the purpose of regulating the temperature of the water or other liquid in the meniscus tube t_1. The letters J_2, I_2, O_2 have a similar significance with respect to the meniscus tube t_2. The letters T_1, T_2 designate thermometers which serve to indicate the temperatures of the liquids in the menisci tubes t_1, t_2.

The manometer is mounted on a slate frame which is supported in a vertical plane perpendicular to the axis of the magnet by a suitable cast-iron structure, the latter being bolted to the cement base upon which the magnet rests.

The method of operation of the balance is exemplified by the procedure followed when pure water is under experimentation. While the temperatures of the water in the menisci tubes t_1, t_2 are maintained at the standard temperature T_0, the positions of the menisci m_1, m_2 are varied until a balance is obtained as estimated by the lack of motion, upon throwing on and off the magnetic fields, of the suspended particles in the capillary tube, observed through the microscope *Mic*. The two magnetic fields acting upon the menisci m_1, m_2 are then the same, H_0, say. These positions of the menisci are called their zero-positions. Upon changing the temperature of the water in the meniscus tube t_1, the balance is destroyed; a new balance is obtained upon moving the meniscus m_2 (by varying the currents through coil 1 and coil 2) through a distance D, say, into a slightly stronger or weaker field H, say, as required. During this procedure the meniscus m_1 is kept in its fixed zero-position. The distance D through which the meniscus m_2 is moved in order to effect a balance is measured by the micrometer telescope focussed upon it.

The field H relative to H_0 is derived from a calibration curve, obtained by substituting for the water in the left-branch dilute solutions of nickel chloride at the temperature T_0 and of different known concentrations.[3]

SENSITIVITY OF BALANCE

In calculating the sensitivity of the balance, we suppose that the water columns in the menisci tubes have the same cross sections, a; that the mercury columns in the bulbs E_1, E_2, have the same cross sections b; and that the water column in the capillary tube *Cap* has a cross section c. Furthermore, we suppose that the menisci tubes are each inclined downwards at an angle θ to a horizontal plane.

Assuming an initial state of equilibrium, if we let Δl denote the apparent displacement, observed in the microscope *Mic*, of a suspended particle in the capillary tube *Cap* due to a difference of pressure Δp on the menisci m_1, m_2, then the sensitivity S, say, of the balance will be proportional to $\Delta l/\Delta p$. A simple calculation shows that:

$$S = \frac{\alpha}{g}\,\frac{a}{c}\left[\rho_m\frac{a}{b} - \rho_w\left(\frac{a}{b} + \sin\theta\right)\right]^{-1} M, \tag{1}$$

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[3] The method does not require a knowledge of the absolute values of H and H_0; in our experiments these values were probably in the neighborhood of 18,000 c.g.s. units.

where α is the factor of proportionality, g the acceleration due to gravity, ρ_m, ρ_w the densities of mercury and water, respectively, and M the magnifying power of the microscope. It can also easily be shown that the condition for stable equilibrium is:

$$\sin\theta < (a/b)(\rho_m/\rho_w - 1).$$

For the special case in which the menisci tubes are horizontal we have $\sin\theta = 0$, and hence:

$$S = \alpha(b/c)(\rho_m - \rho_w)^{-1}M. \tag{2}$$

For the balance used in our experiments: $\theta = 0$, and $a = 0.070$, $b = 34.0$, $c = 0.0064$, $M = 400$, $\rho_m = 13$, $\rho_w = 1$, approximately, in c.g.s. units. The proportionality factor α could be determined without great trouble if desired.

The sensitivity of the balance used by us is such that changes in the susceptibility of water as small as one ten-thousandth part can easily be detected.

We estimate, with the aid of Eq. (2), that the sensitivity of our balance could easily be increased one thousand times but, owing to vibrational disturbances, this would not be feasible.

THEORY OF THE METHOD

Let κ, κ_0 designate volume susceptibilities of water at the temperatures T, T_0. When balance obtains:

$$\tfrac{1}{2}\kappa H_0^2 = \tfrac{1}{2}\kappa_0 H^2.$$

If χ, χ_0 denote specific susceptibilities and ρ, ρ_0 densities of water at the temperatures T, T_0, then $\kappa = \rho\chi$ and $\kappa_0 = \rho_0\chi_0$; and hence:

$$\chi/\chi_0 = (\rho_0/\rho)(H^2/H_0^2). \tag{3}$$

We now recall that H_0 represents strength of the magnetic field at the meniscus m_1 in its zero-position, while H represents the strength of the magnetic field acting on the meniscus m_2 when it has been displaced from its zero-position by the amount D, say, necessary to obtain the balance. When the quantity $\rho_0 H^2/H_0^2$ as a function of D is known, formula (3) can be used to calculate the ratio χ/χ_0, the density ρ being taken from a table for water. A calibration curve giving this quantity as a function of D is obtained as follows:—

A water solution of nickel chloride is prepared which is neutral at the standard temperature T_0 (23.5°C). From this neutral solution several diamagnetic solutions are made, each of which is prepared by adding to a mass m of the neutral solution a mass μ of water, so that the total mass of the diamagnetic solution is $m+\mu$. If χ_n denote the specific susceptibility of such a diamagnetic solution at the standard temperature T_0 and χ_0 that of pure water, then by Wiedemann's law:

$$(m + \mu)\chi_n = \mu\chi_0.$$

Hence:

$$\chi_n/\chi_0 = 1/(1 + \delta), \text{ where: } \delta = m/\mu. \tag{4}$$

If such a diamagnetic solution be introduced in the left branch of the balance with its meniscus m_1 in the field H_0, and if the right branch contain water with its meniscus m_2 in a field H which is such as to give a balance when the two liquids are at the standard temperature T_0, then it is evident from Eq. (3) that:

$$\chi_n/\chi_0 = (\rho_0/\rho_\delta)(H^2/H_0^2), \tag{5}$$

where ρ_δ denotes the density of the diamagnetic solution at the standard temperature T_0. Hence from Eqs. (4) and (5):

$$\frac{\rho_0 H^2}{H_0^2} = \frac{\rho_\delta}{1+\delta}\,. \tag{6}$$

Now, supposing the values of δ and ρ_δ to be known, if D denote the necessary displacement of the meniscus m_2 from its zero-position in order to obtain a balance, and if the values of D for several diamagnetic nickel-chloride solutions are known by experiment, a calibration curve can be constructed with the quantity $\rho_0 H^2/H_0^2$ plotted against D.

From the calibration curve the values of the quantity $\rho_0 H/H_0^2$ can be taken for use in Eq. (1), after the value of D has been found for the case in which water at temperature T is balanced against water at the standard temperature T_0.

CALIBRATION OF THE BALANCE

The data used in the construction of a typical calibration curve are given in Table I. The quantity δ represents the ratio of a mass m of neutral solution to the mass of water μ added to it in forming the diamagnetic solutions numbered 1, 2, · · · 6; ρ_δ represents the density of a diamagnetic solution at the standard temperature T_0 (23.5°C); and D represents the displacement of the meniscus m_2 from its zero-position, expressed in terms of head divisions of the micrometer telescope focussed upon it, in order to produce a balance of a diamagnetic solution against water at the standard temperature T_0.

TABLE I.

Solution number	δ	ρ_δ	D	$\rho_\delta/(1+\delta)$
1	0	0.99742	0	0.99742
2	0.003749	0.99750	65	0.99377
3	0.007516	0.99758	119	0.99014
4	0.011241	0.99767	175	0.98658
5	0.014999	0.99775	236	0.98301
6	0.018767	0.99783	316	0.97945
7	0.026858	0.99800	413	0.97190
8	0.031305	0.99806	484	0.96776

A calibration curve constructed with the aid of these data is shown in Fig. 3. It is the one used in the construction of curve 2 shown in Fig. 4.

RESULTS

In Fig. 4 there are shown two curves, one labelled curve 1 and the other curve 2. In the case of each curve the ratio of the specific susceptibility of water at temperature T to that at 20°C, is plotted against the temperature, the temperature 20°C being chosen instead of 23.5°C as the standard temperature in order to facilitate comparisons with the curves of Fig. 1.

The figures associated with the observation points on each curve indicate the corresponding observation times reckoned in minutes from the time at which the zero adjustment of the manometric balance was made. The significance of these annotations will presently become apparent.

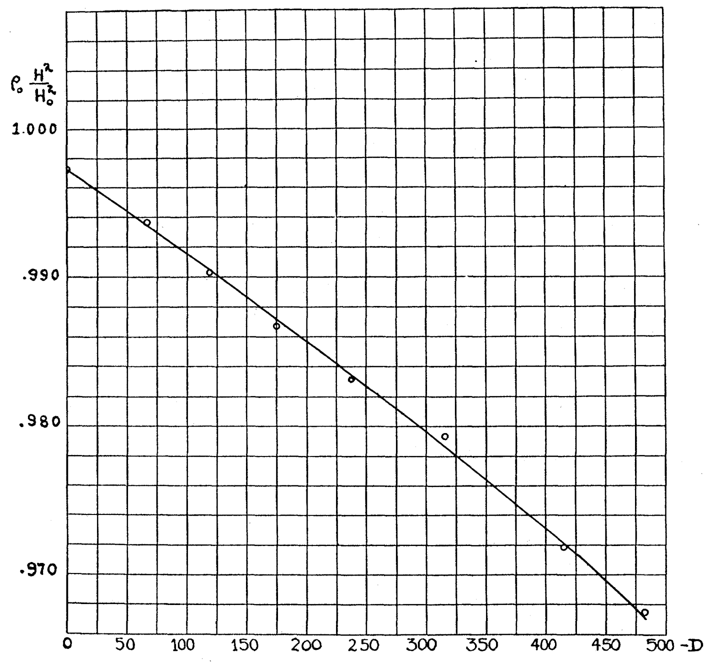

Fig. 3. Calibration curve.

The two curves have certain characteristic features in common, notably the correspondence of maxima and minima points. They differ essentially, however, in that curve 1 indicates that at higher temperatures the diamagnetism of water is *less* than at our standard temperature 23.5°C, while curve 2 indicates that it is *greater*. Each curve was satisfactorily checked by an independent run under corresponding conditions.

The results represented by curve 1 might be cited in support of those found by Cabrera and Duperier (1925), while the results represented by curve 2 might be cited in support of those found by Piccard and Johner (1930); in fact, for temperatures up to 40°C the agreement of curve 2 with the corresponding curve of Piccard and Johner (see Fig. 1) is rather good.

Since the sensitivity of the manometric balance is such as to permit easy detection of changes in relative susceptibility of the order 10^{-4}, the differences between curve 1 and curve 2 must be looked for elsewhere than in the errors of observation.

Various experiments led us finally to the conclusion that these differences have their origin in differences in the procedures followed in preparing the samples of water used in the two sets of experiments.

The water used in both sets of experiments was distilled in the apparatus of the Department of Chemistry, Columbia University. That used in the first set was afterwards boiled vigorously for about 15 minutes in a Pyrex container just before the experiments whose results are represented by curve 1 were begun. The water used in the second set of experiments was similarly prepared, except that after boiling it was sealed in its container after the air therein had been displaced by helium gas and then left to stand for 3 days before using. Throughout each set of experiments the water was kept in contact with helium gas with no air present.

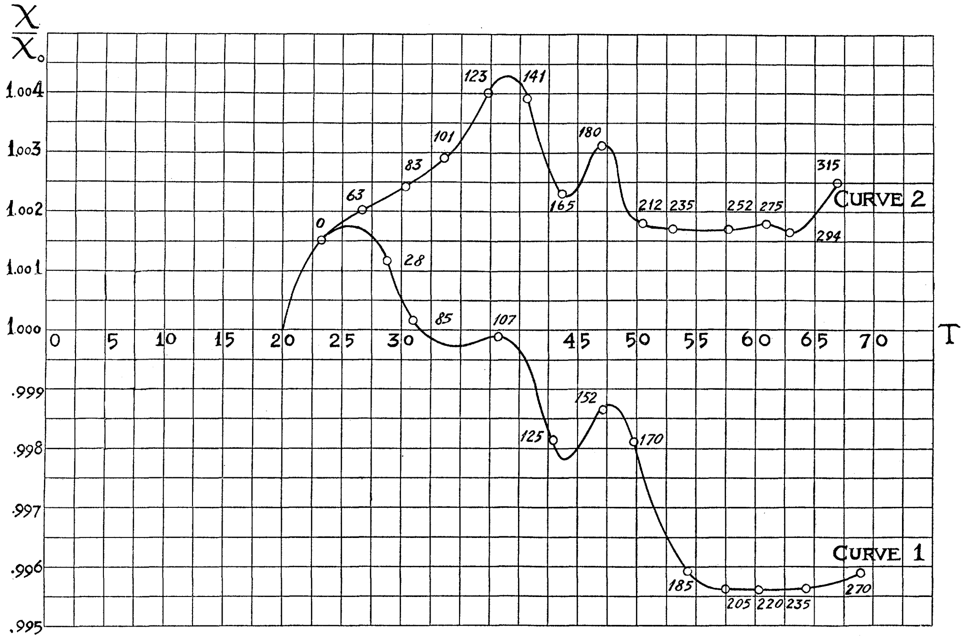

Fig. 4.

The calibration curve used in the construction of curve 1 was obtained by balancing diamagnetic nickel chloride solutions which had stood for several days in contact with helium gas against recently boiled water at the standard temperature 23.5°C, and the calibration curve used in the construction of curve 2 was obtained in the same way, except that the water used had stood for several days in contact with helium gas.

We are now of the opinion that curve 2 approximates fairly closely a true equilibrium curve, but further rather lengthy experiments will have to be carried out before this opinion can be fully substantiated.

The observations upon which curve 2 was constructed are recorded in the first three columns of Table II, captioned respectively T, $H \cdot D$, and $T \cdot E$; the first column contains the values of the temperatures at which the observations were made expressed on the centigrade scale; the second column contains the values of the displacements of the meniscus m_2 from its zero position expressed in terms of head divisions on the micrometer telescope focussed upon it; the third column contains the values of the times elapsed expressed in minutes reckoned from the time at which zero adjustment of the manometric balance was made. In the fourth column are found the values in c.g.s. measure of the quantity which captions it, taken from a calibration curve whose derivation is explained above. The fifth column contains the values for the densities of water at the corresponding temperatures. In the sixth column are found the ratios of the specific susceptibilities of water at temperatures T to its specific susceptibility at the temperature 23.5°C.

Table II.

T	$H \cdot D$	$T \cdot E$	$\rho_0 H^2/H_0^2$	ρ	χ/χ_0
23.50	0	0	0.99742	0.99742	1.0000
26.80	6	63	0.99710	0.99660	1.0005
30.45	18	83	0.99640	0.99554	1.0008
33.90	28	101	0.99579	0.99443	1.0013
37.45	30	123	0.99565	0.99318	1.0024
40.60	51	141	0.99440	0.99201	1.0024
43.85	98	165	0.99145	0.99070	1.0007
46.90	106	180	0.99100	0.98944	1.0015
50.50	145	212	0.98860	0.98784	1.0007
53.50	176	235	0.98670	0.98646	1.0002
57.60	210	252	0.98480	0.98455	1.0002
61.00	238	275	0.98300	0.98272	1.0002
63.00	260	294	0.98180	0.98167	1.0001
66.70	280	315	0.98060	0.97966	1.0009

As regards the numbers in the last column of this table, we estimate that, as far as our actual observations are concerned, they may be in error one way or the other by 1 or 2 units in their last places.

The curve shown in Fig. 5 represents the results of a cyclic run on water which, after boiling, was left for several days in contact with helium gas. The figures associated with the observation points have the same significance as with curve 1 and curve 2, Fig. 4.

An entirely reliable interpretation of the anomalies in the results represented by the curves in Fig. 4 and Fig. 5 cannot, we believe, be given at present. We are confident, however, that the apparently anomalous behavior of water as indicated by these curves cannot be ascribed to errors of observation or to peculiarities of the apparatus; for the susceptibility-temperature curves for benzene and for toluene show no such anomalies.

Questions arise, of course, as to whether the curves for water represent reliable values for the diamagnetism of water or values vitiated by the action (catalytic, perhaps) of unknown impurities or, possibly, by some unsuspected action of a magnetic field upon the surface tension of water, although action of this sort has been fruitlessly sought by various investigators.

If, however, it be granted that the results represented by the curves in Fig. 4 and Fig. 5 are trustworthy, they might, we believe, be explained on the assumption that polymerization changes in water produced by variation in temperature required for their completion a considerable time; but such an assumption is difficult to justify on theoretical grounds.

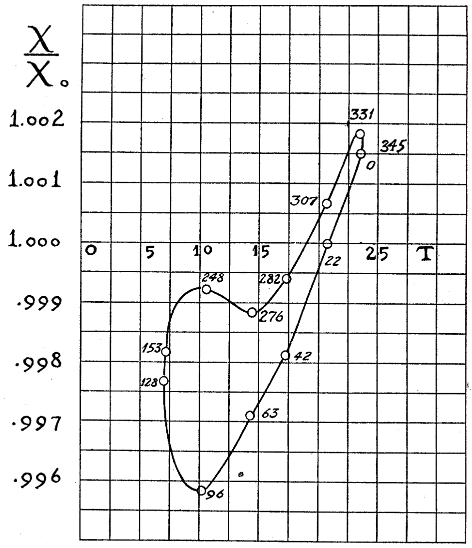

Fig. 5. Cyclic run for water.

A more exhaustive investigation, suggested by the results of our preliminary investigation, will be undertaken in the near future.

We wish to express our appreciation of the very helpful collaboration of Mr. Donald Woodbridge during the later stages of the present investigation.