The Dependence of the Diamagnetism of Water upon Its Temperature

A. P. WILLS AND G. F. BOEKER, *Columbia University*
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The anomalous results described in a previous communication are explained in part, and the results of recent experiments relating to the dependence of the specific susceptibility (χ) of water upon its temperature are given. For the temperature range from 20°C to 66°C these results are represented with fair approximation by the parabolic formula:

$$\chi/\chi_{20}=1+1.3\times10^{-4}(T-T_{20})-0.7\times10^{-6}(T-T_{20})^2.$$

A comparison is made of the results obtained with those found by previous observers.

IN a former communication[1] a new instrument for the measurement of the magnetic susceptibilities of liquids at different temperatures was described, and some preliminary results obtained in experiments on water were given. These results were anomalous in several respects, however, and the anomalies at the time seemed very puzzling and difficult to explain. It was suggested that the source of these anomalies might possibly be found in the differences in the thermal history of the water used in the various experiments, but subsequent experiments have shown that the anomalous effects previously observed were such as to preclude explanation on such an assumption.

Chief among the anomalies in question were the results of a susceptibility-temperature run on recently boiled water which incorrectly indicated decreasing diamagnetism with increasing temperature. In a recent paper[2] and in private communications H. Fahlenbrach has suggested a possible explanation of this anomaly based upon the assumption that the calibration of our instrument might have been at fault because of the possibly unwarranted reliance which we placed upon our method of calibration, which is fully described in our earlier paper. Although we are now certain that the explanation of Fahlenbrach is not tenable, the points which he raises are of sufficient importance to warrant mention. Our method of calibration depends upon the measurement of a magnetic field gradient by means of test aqueous nickel chloride solutions whose magnetic susceptibilities at a standard temperature are determined experimentally in terms of that of pure water at the same temperature as follows: A given test solution is prepared by first making up a magnetically neutral solution of nickel chloride in pure water at the standard temperature and then mixing with a mass m of this solution a mass μ of pure water. If χ_n and χ_{20} denote the specific susceptibilities of the test solution and of pure water at the standard temperature (20°C), we then make the assumption (Wiedemann's law) that:

$$\chi_n=[\mu/(\mu+m)]\chi_{20}.$$

It is the validity of this equation which is in effect questioned by Fahlenbrach, who has shown that the magnetic moment of the nickel ion of nickel chloride in solution may not have a determinate value, since it may depend upon the method of preparation of the solution and upon its concentration. Using our original apparatus, Mr. Donald Woodbridge has shown, however, that the method followed by us in the preparation of our test solutions is not subject to errors of the sort suggested by Fahlenbrach.

Eventually, we were led to the conclusion that our results indicating decreasing diamagnetism of water with increasing temperature could be explained only upon the assumption of an unsuspected leak of air into the vessel containing the helium gas against which the susceptibility of the water was to be measured; and that the anomalies in the results represented in Fig. 5 of our earlier paper might be accounted for likewise. Calculation shows that the effects in question could be thus explained.

[1] A. P. Wills and G. F. Boeker, Phys. Rev. **42**, 687, (1932).
[2] B. Cabrera and H. Fahlenbrach, Zeits. f. Physik **82**, 759 (1933).

Further experiments with our original apparatus showed that it could be modified advantageously in several details, and it was finally decided to construct an entirely new instrument upon the same basic principle[3] with which to continue our susceptibility-temperature investigations on water. In course of time this instrument was completed; it constitutes a manometric magnetic balance so simple and compact in design that we are confident it would prove a highly satisfactory instrument for physicists and chemists engaged in the study of the magnetic properties of liquids; it is proposed to give a detailed account of this instrument in a separate communication.

Results of Recent Experiments

Using the new balance, we have made further measurements of the magnetic susceptibility of water at different temperatures. The results for the specific susceptibility ratio χ/χ_{20}, where χ denotes the susceptibility at a temperature T and χ_{20} the susceptibility at 20°C (T_{20}), were furnished by nine individual susceptibility-temperature runs comprehended in the temperature interval from 20°C to 66°C. A typical run over this entire range is represented by a zigzag line in Fig. 1, constructed by joining consecutive experimental points by straight-line segments. By averaging curves of this sort for the nine runs the curve in Fig. 1 with the legend *average of runs* was obtained.

Our experimental results for the temperature interval specified above are on the whole fairly well represented by the parabolic formula:

$$\chi/\chi_{20}=1+1.3\times10^{-4}(T-T_{20})-0.7\times10^{-6}(T-T_{20})^2,$$

where χ, χ_{20} denote the specific susceptibilities of water at the temperatures T, T_{20}. The full-line curve in Fig. 1 is a graph of the parabola represented by this equation; 33 experimental values

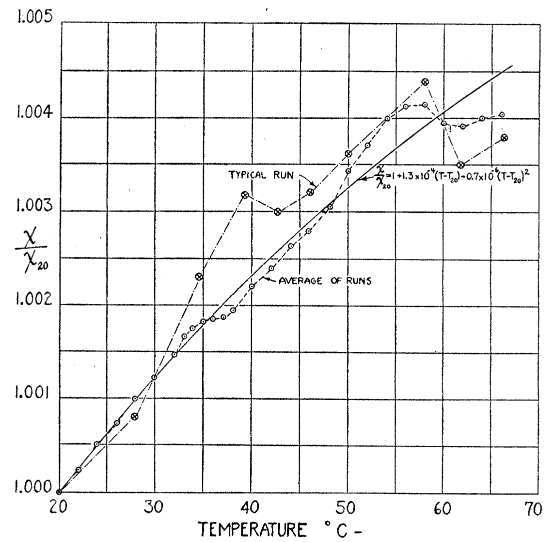

FIG. 1. Variation of susceptibility of water with temperature.

of the quantity χ/χ_{20} are represented by points which lie above this curve and 34 experimental values by points which lie below it. The average plus and minus deviations of these points from the curve and the corresponding maximum deviations, determined with the aid of a large-scale graph, are as follows:

average + deviation	+0.000365,
maximum + deviation	+0.00097,
average − deviation	−0.000365,
maximum − deviation	−0.00094.

Each individual run shows, however, a definite break in the slope of the susceptibility-temperature curve in the neighborhood of 35°C and another, more significant, in the neighborhood of 55°C; the average effects of these breaks is apparent from the curve in Fig. 1, representing the average of nine runs. It is possible that these breaks indicate significant changes in molecular arrangement or association of the water molecules.

The temperature coefficient at 20°C for the quantity χ/χ_{20} has been estimated with the aid of a large-scale graph of our experimental results to have the value 1.30×10^{-4}.

Our method is not subject, we believe, to many systematic errors, and those which must be most carefully guarded against have their origin in anomalous conditions which sometimes appear at the free surfaces of the liquids in the menisci

[3] The principle upon which our instrument operates depends upon balancing the force exerted by a magnetic field upon a standard liquid of known susceptibility, contained in a Pyrex tube of small diameter with its free surface (meniscus) at a fixed position in the field, by a corresponding force exerted by a second magnetic field upon the liquid whose susceptibility is to be measured and contained in a similar tube, balance being effected by moving the meniscus of this liquid to a determined position in the second field, whose gradient along the tube is known, such that the two forces equilibrate.

tubes and which manifest themselves by "sticking" or "drifting" of the menisci of the liquids; these conditions occasionally arise despite great care used in cleaning the menisci tubes and in the temperature control of the liquids themselves, particularly at the higher temperatures. As a result of long experience we now know that measurements made when there is any evidence of sticking or drifting are probably erroneous and should be rejected.

Comparison of Results of Different Observers

Comparison of the results obtained by different observers[4] for the magnetic susceptibility of water as a function of its temperature shows on the whole a not very satisfactory agreement. At room temperature, however, the agreement among the numbers found by a considerable number of observers for the temperature coefficient of the susceptibility ratio χ/χ_{20} is reasonably satisfactory, as is apparent from Table I.

Marke, Johner, and Cabrera and Fahlenbrach found the temperature coefficient for the quantity χ/χ_{20} to be independent of the temperature within the precision of their measurements.

In the temperature interval from 20°C to 65°C the results of Piccard and of Auer are in remarkably good agreement. For the same temperature interval our results indicate somewhat larger values for this quantity than those obtained by them, the greatest difference occurring at about 57°C, at which we find the value 1.0042 for the ratio χ/χ_{20} and Auer finds 1.0035; at this temperature, however, our value is in excellent agreement with those found by Marke and by Cabrera and Fahlenbrach.

For the temperature interval from 20°C to 0°C the values found by Piccard and by Auer for the quantity χ/χ_{20} diverge more and more as the temperature decreases, those of Piccard being notably higher. Because of difficulties connected with the condensation of water vapor on the colder of the meniscus tubes of our apparatus owing to the high humidity incident to summer weather we were forced to defer making measurements at temperatures below 20°C to a more favorable season.

Table I.

Observers	$\frac{1}{\chi_{20}}\frac{d\chi}{dT}\times 10^4$
Piccard (1913)	1.20
Marke (1916)	1.17
Piccard and Johner (1930)	1.3_1
Cabrera and Fahlenbrach (1933)	1.15
Auer (1933)	1.26
Wills and Boeker (1934)	1.30

[4] For a detailed comparison of the results obtained by Auer and by previous observers and for references the following paper may be consulted: H. Auer, Ann. d. Physik **410**, 593 (1933).