The heat capacity data and the temperature change during magnetization have been used to calculate the entropy change accompanying isothermal magnetization. Values of this quantity have been used, in combination with thermodynamic relationships, to evaluate the temperature coefficient of magnetic susceptibility.

A curve of the initial magnetic susceptibility calculated by integrating the temperature coefficient of susceptibility is in complete agreement with the directly measured values.

The portion of the total heat capacity due to the electronic system has been estimated by comparing the data with the heat capacity of the diamagnetic zinc sulfate heptahydrate. Near the liquid helium temperature region the rather considerable heat capacity is almost completely due to the electronic system.

The relationship between the observed heat capacity and the electronic energy pattern responsible for it has been discussed.

The heat capacity of Pyrex glass below 20°K. has been estimated as $1.07 \times 10^{-6}T^3$ cal. g.$^{-1}$ deg.$^{-1}$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Measurement of Magnetic Susceptibility at Low Temperatures[1]

BY W. F. GIAUQUE, J. J. FRITZ AND D. N. LYON

The purpose of this paper is to describe a fluxmeter arrangement for measuring adiabatic differential magnetic susceptibilities in the region near and below 1°K. The particular instrument to be described here has been used for a research on cobaltous sulfate heptahydrate[1a] and is now in use for additional investigations in this Laboratory. For this reason, and also to separate the account from other experimental details, it has seemed desirable to give a description which can be used as a common reference in the recent and future work.

A fluxmeter is simple in principle, being based on the fact that a coil surrounding a sample will acquire an e. m. f. when a change in magnetic induction occurs within the coil. This principle is sometimes used in rough experiments in which a piece of magnetized iron is suddenly withdrawn from a coil which is attached to a ballistic galvanometer. In the present work it is very desirable not to move the sample which is surrounded by a vacuum jacket and attached to various electrical leads and other experimental facilities. Moreover the measurement of the deflection of a ballistic galvanometer is nowhere near a sufficiently accurate procedure to meet the requirements of adiabatic demagnetization work. The sample may be left stationary if the space occupied by the sample and its surrounding coil is in turn surrounded by an exciting coil which serves to produce a sudden change in magnetic induction. This requires the evaluation of the induction which would cut the coil if the sample were absent. This may be done most simply in this type of investigation by heating the sample (but not the coil) until the susceptibility is so reduced that it can be considered as a small correction. In order to obtain accuracy the e. m. f. induced in the sample coil must be measured by an essentially null point method. An arrangement for doing this has been described and used by Giauque and Stout[2] who used a set of standard coils mounted within a second exciting coil to balance the effect of the sample coil. In their arrangement the two exciting coils were connected in series and in order to avoid magnetic interference the standard fluxmeter arrangement was located in an adjacent room well away from the adiabatic demagnetization apparatus. The major problem in any null point method arises from the fact that the two e. m. f.'s must be balanced not only in magnitude but in phase if a sensitive galvanometer is to be used.

If magnetic properties are to be investigated as a function of magnetic field, the experimental arrangement must be mounted within a magnet. This requires the presence of considerable amounts of metal near the sample and the coil surrounding it. The time required for the exciting coil to produce its change in magnetic induction will be increased by the opposing effects of various currents which are simultaneously induced in any metal objects which are within effective range of its field. Giauque and Stout[2] solved this problem so far as the measurement of initial magnetic susceptibility was concerned by placing duplicate metal parts in the same relative positions with respect to the standard fluxmeter coils and their exciting coil. They also remark "The sample and the opposing coils could be located within the same exciting magnet provided they are sufficiently isolated from each other. There are, however, some objections to this, especially in connection with low temperature investigations where the space in and near the magnet is more valuable for other purposes. Moreover, it is desirable to keep the standard coils at a fairly constant temperature to prevent dimensional changes." This latter point is the most important one because the change in turn area, when a coil is cooled from ordinary

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[1] This work was supported in part by the Office of Naval Research, United States Navy.

[1a] Fritz and Giauque, THIS JOURNAL, 71, in press (1949).

[2] Giauque and Stout, *ibid.*, 61, 1384 (1939).

temperatures to the temperatures of liquid helium, is considerable and not necessarily highly reproducible.

It is obvious that the phase difficulties can be reduced most simply by having the opposing coils in essentially the same environment. Moreover this would help eliminate such effects as those due to resistance changes accompanying temperature variations of the metal parts of the magnet which are quite appreciable during its operation.

The present arrangement is an extension of the fluxmeter mentioned above. Briefly it consists of the previous arrangement plus a set of secondary reference coils located within the magnet and immersed in the liquid helium-bath. They are located a short distance below the sample coils and have in fact been placed close enough to the sample so that they are somewhat influenced by it, requiring a small correction, which can be obtained either by calculation or direct measurement.

This arrangement is designed to do more than overcome the particular magnetic induction timing difficulties mentioned above. There is another factor which complicates the use of the original fluxmeter arrangement with the sample in a magnetic field. When the solenoid magnet circuit is closed, as it must be when a field is produced, this circuit couples with the coil about the sample. This throws the e. m. f. induced in the sample coil out of phase with the e. m. f. from the fluxmeter by an amount which depends on the particular resistance and field in the magnet circuit. The use of the earlier arrangement was practically restricted to the measurement of initial susceptibility. Values within a field were obtained by means of an inductance bridge method of inferior accuracy.

With secondary reference coils placed near the sample as mentioned above, the accurate measurement of adiabatic differential susceptibilities in strong fields has become possible with the fluxmeter arrangement when storage cells are used to supply the magnet current. In this case it is also possible to use a small change in the magnet current to replace the exciting coil of the fluxmeter. In fact this is the procedure which is actually used to make measurements in the magnetic field since it is impractical to have the fluxmeter coil system balance simultaneously with respect to both the magnet solenoid and the separate exciting coil of the fluxmeter. If the system is balanced with respect to the exciting coil, a fluctuation in the magnet current will cause a disturbance. However, if the fluxmeter system is balanced with respect to the magnet solenoid, a small fluctuation or drift in magnet current will produce a negligible effect.

The exciting coil is usually used for measurements of the initial susceptibility and the magnet solenoid is always used to excite the fluxmeter for measurements in the presence of magnetic fields. It is of course necessary to calibrate the fluxmeter coils with respect to each different exciting coil used since the product of turn area times field for each coil will be slightly different. The necessary small change in magnet current was produced by shunting a suitable resistance across the magnet. The resistance of this shunt was variable so that the sensitivity of the fluxmeter could be selected. It was found that the motor-generator supply of current available to us contained too many violent disturbances to be sufficiently balanced out. Perhaps it should be mentioned that the available source is a general supply line with numerous other uses which produce disturbances aside from those resulting from the motor generator unit. Nevertheless fluctuations in the generator itself are undoubtedly serious. These can be minimized by floating storage cells, with sufficient capacity, on the generator circuit.

Another advantage of the secondary reference coils is that they can be made almost identical with the coils about the sample. It is necessary to keep the resistance in the fluxmeter circuit low so that good galvanometer sensitivity can be obtained. The resistance of the copper wire drops to such low values at low temperatures that large numbers of turns of very small wire can be used. In the case of the primary fluxmeter coils which are kept at room temperature, the coils must be made of much larger wire, and of larger diameter, to minimize resistance. As a consequence their interaction with surrounding metal is slightly different than that of the compact low temperature coils and the opposing e. m. f.'s are not as precisely balanced as in the case where the coils are nearly identical.

It would be rather impracticable to use the above arrangement without having samples which are ellipsoids of revolution since it is only in this case that the equations can be solved for obtaining the susceptibility in terms of the magnetic induction cutting the reference coils.

The Schematic Arrangement.—A schematic diagram giving the essentials of the fluxmeter arrangement is shown in Fig. 1. E, E show end-portions of the continuous helical exciting coil within the magnet. This is coaxial with the sample and the sample coil, G, and the secondary reference fluxmeter coils, J. The primary standard fluxmeter exciting coil is shown in part at F, F. It encloses the standard coils I which are coaxial with it. The two exciting coils and their enclosed apparatus are located well away from each other's influence. In the present case they are located in different rooms some 35 ft. apart.

The exciting helical coils E and F are each made long in comparison with the enclosed coils so that the effective field is quite homogeneous although some small variation in field intensity makes little difference since the autocalibration takes the product of turn area times field into account. However the turn area of the coil about the sample must be accurately known in order to standardize the other coils. This standardization was made before the sample coils had been cooled, because at this time their dimensions were most accurately known. By means of the standardization information then preserved in the primary fluxmeter coils which may be thermostated if necessary it was found that the sample coils lost about 0.1% of their turn area after being cooled to liquid helium temperatures and rewarmed to room temperature.

The experimenter observes the high sensitivity galvanometer, C, as he makes or breaks the exciting coil current by means of the key, A, in the circuit with some source such as the storage cells shown at B. An ordinary direct current supply line is also satisfactory for this purpose. The sample coil, G, can be connected in opposition to a sufficient number of the intermediate reference coils, J, so that an almost null reading is obtained. It is desirable to alter the coils, J, by adding or subtracting a small coil so as to determine the sensitivity of the arrangement and thus enable correction for the small deflections when the key is pressed or released.

The arrangement is sufficiently sensitive so that it can be affected by fluctuations in the earth's magnetic field and the coils should be connected so as to cause cancellation of this effect. Coils G and J must be used in opposition so that this effect is naturally eliminated. However, when coils I are used in opposition to coils G they should be connected to effect this cancellation. Similarly when coils J are measured by means of coils I they should be arranged so as to balance out this effect. If exciting coils E and F are connected so that their magnetic fields are both permanently directed, either up or down, cancellation with respect to the fluctuations of the earth's field will be achieved by any workable arrangement of the other coils. Opposing the coils of I to coils J requires the use of a reversing switch which has been left out of Fig. 1 to simplify the diagram. When coils G are opposed to coils J, coils I are shunted out by closing switch D. When coils I are opposed to coils J, switch H is thrown to the right to eliminate coils G. To measure coils G by means of fluxmeter coils I, the switch K is closed to shunt out coils J.

Coils I remain at room temperature and thus retain constant dimensions. Coils G and J are ordinarily cooled to liquid helium temperature and must be calibrated in terms of coils I after coils G and J have become stabilized at that temperature. Coils J can be autocalibrated while they are in the helium-bath so that in principle only one standard coil I would be necessary; however, it has been found that a full range set of coils I is convenient.

Introducing coils J into the liquid helium-bath has made it necessary to run a large number of electrical leads into the bath. Although some 30 no. 36 copper wires have been run into the helium-bath, the heat transfer between the wires and the helium gas in the upper portions of the Dewar vessel has prevented any serious heat leak into the liquid helium.

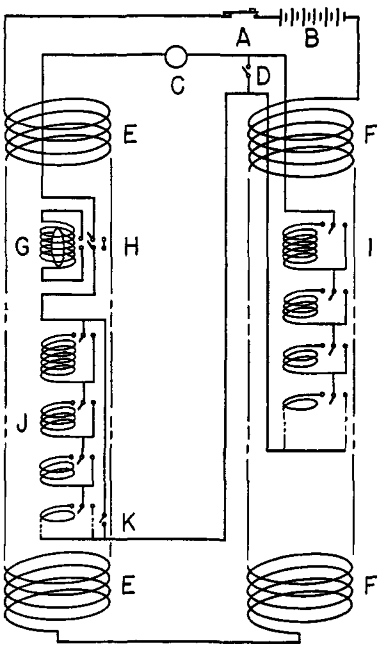

Fig. 1.—Low temperature double fluxmeter: secondary reference coils at low temperatures within same heavy metal environment as sample.

Cadmium–Zinc Solder.—While it is best to have long leads on coils G and J, so that any soldered connections will be well removed from the coil system, it will be convenient to be able to make small soldered connections near the coils in case a wire breaks. Since both lead and tin are superconductors, the use of ordinary solder could produce small disturbing effects due to their perfect diamagnetism in low fields and its sudden disappearance above the threshold field values for these substances.

There are no low melting elements which are non-superconductors and which are sufficiently inert chemically to recommend their use as components in a low melting solder. However, Kurti and Simon[3] have found that cadmium is not a superconductor above 0.54°K. and Keesom[4] found the transition point of zinc to be 0.79°K. Since each of these temperatures is below the helium-bath temperatures used in adiabatic demagnetization investigations, it appeared that the cadmium–zinc eutectic mixture might be a satisfactory solder to use in low temperature magnetic investigations. The eutectic temperature is 263° and the composition is 83% cadmium.[5] We have tried soldering small copper

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(3) Kurti and Simon, *Proc. Roy. Soc. London*, **151A**, 610 (1935).

(4) Keesom, *Physica*, **1**, 123 (1934); Comm. Phys. Lab. Univ. Leiden, 230 a.

(5) "International Critical Tables," Vol. II, McGraw-Hill Co., New York, N. Y., 1926, p. 436.

wires together with cadmium–zinc solder and find that it is quite satisfactory for this purpose. Rosin was used as a flux and some care should be taken to avoid overheating.

The Low Temperature Fluxmeter.—A scale drawing of the low temperature fluxmeter is shown in Fig. 2. The coils L, L are coaxial with the ellipsoidal sample M. They were placed symmetrically one above and one below the equatorial plane of the ellipsoid. A spacer, N, 2 mm. thick, was left between the coils to strengthen the Dilecto tubing of which the entire coil support was constructed. The Bakelite impregnated molded paper (Dilecto) tubes were selected as coil supports because it has been found[2] that its average coefficient of expansion over the region between the temperatures of liquid helium and ordinary temperatures is approximately the same as that of copper.

The coil about the sample is made in two parts so that they can be used in opposition to cancel out irregularities in large fields when measurements are made with an inductance bridge. This arrangement has been described previously by Giauque, Stout, Egan and Clark.[6]

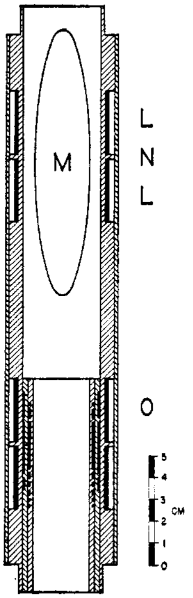

Fig. 2.—Low temperature coils of double fluxmeter.

The coils were wound with no. 36 B. and S. gage double enamelled copper wire as in the case of previous sample coils. The lower set of coils, O, which serve as the secondary reference coils of the fluxmeter, consists of 13 coils. The outer two were wound on the same form as the sample coils and were made as identical to these as possible. The remaining 11 coils were wound on two Dilecto forms which telescoped inside the outer form. These coils contained from 1 to 300 turns; in general each coil had approximately twice the turn area of the one next smaller. This set of fluxmeter coils was centered about a point 13 cm. below the center of the sample. All of the coil supports were held rigidly together by means of Micarta set screws, which are not shown.

TABLE I

SECONDARY FLUXMETER COIL CONSTRUCTION DATA

Coil	No. of layers	Total no. of turns	i. d., cm.	o. d., cm.
Sample 1	12	2210	3.967	4.285
Sample 2	12	2218	3.967	4.287
Fluxmeter 1	12	2205	3.967	4.293
Fluxmeter 2	12	2188	3.967	4.298
Fluxmeter 3	2	300	3.332	3.393
Fluxmeter 4	2	272	2.795	2.856
Fluxmeter 5	2	144	3.332	3.393
Fluxmeter 6	2	72	3.332	3.393
Fluxmeter 7	2	58	2.795	2.856
Fluxmeter 8	2	28	2.795	2.856
Fluxmeter 9	2	14	2.795	2.856
Fluxmeter 10	1	7	2.795	2.825
Fluxmeter 11	1	4	2.795	2.825
Fluxmeter 12	1	2	2.795	2.825
Fluxmeter 13	1	1	2.795	2.825

Turn area of sample coil No. 1, 29,390 sq. cm. at 298°K.

Turn area of sample coil No. 2, 29,498 sq. cm. at 298°K.

Root mean square radius, both coils, 2.057 cm.

Details of the construction of the coils are given in Table I. All coils were wound as closely as possible, and the number of turns per layer was maintained as constant as the small variations in the diameter of the wire permitted.

The data on the coils of the primary (external) fluxmeter are given in Table II. They were wound of no. 28 B. & S. gage double silk covered wire. Probably double enamelled wire would have been better for this purpose as well as for the low temperature coils. All of the coils were wound on Pyrex glass tubes and the assemblies were 10–12 inches long.

TABLE II

PRIMARY FLUXMETER COIL CONSTRUCTION DATA

Coil no.	No. of layers	Total no. of turns	i. d., in.
1	2	684	4.5
2	2	456	4.5
3	2	228	4.5
4	2	298	3.0
5	2	200	3.0
6	2	100	3.0
7	1	50	3.0
8	1	30	3.0
9	1	20	3.0
10	1	10	3.0
11	1	5	3.0
12	1	3	3.0
13	1	2	3.0
14	1	1	3.0
15	1	2	1.5
16	1	1	1.5

The exciting coils of both fluxmeters were 3 ft. long and the solenoid magnet was also of this length. The exciting coils were wound on Pyrex glass tubing 5.5 inches in diameter. The exciting coil of the primary fluxmeter was wound of no. 24 B. and S. gage double cotton covered copper wire. The similar exciting coil in the magnet was inadvertently made from no. 22 wire instead of no. 24. However this apparently made little difference. The several fluxmeter factors which are determined experimentally take care of any such variations.

The galvanometer was not specially selected since an instrument which happened to be in use for other measurements proved to be convenient

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(6) Giauque, Stout, Egan and Clark, THIS JOURNAL, 63, 405 (1941).

and satisfactory for balancing the fluxmeter. The measurements were made on a high sensitivity galvanometer used with a 100,000 microvolt Leeds and Northrup White Double Potentiometer. The galvanometer had a resistance of 38 ohms, a period of 9.2 seconds and a critical damping resistance of 450 ohms.

The resistance of the coils about the sample decreased from about 750 ohms at room temperature to 11 ohms at the temperature of liquid helium while the secondary reference fluxmeter coils changed from about 850 ohms to 14 ohms. The total resistance of the coils in the primary fluxmeter, which were always at room temperature, was about 172 ohms.

The Calculation of Magnetic Susceptibility from the Measured Magnetic Induction which Cuts the Coils.—Equations for calculating the magnetic susceptibility, χ, from the increase in the magnetic induction through the sample coils due to the presence of the sample in an otherwise homogeneous field H_0, have been given by Giauque and Stout,[2] who give previous references. They considered the case of an ellipsoidal sample surrounded by coils such as the sample coils shown in Fig. 2. An ellipsoidal sample is considered to be introduced into a relatively large region which would be magnetized homogeneously except for the effect of the sample.

The present arrangement is complicated by the fact that the secondary reference coils have been placed rather near to the sample for the reasons given above. Consequently, readings taken in terms of the induction through these reference coils must be corrected for the effect which the sample of unknown susceptibility produces on them. The equations and the interrelationships of the various coils are sufficiently complicated so that a method of approximations should be used. Fortunately the effect of the sample on the secondary reference coils is small so that, after a little experience, the first approximation will be quite accurate. In a recent set of experiments, in which the increase in magnetic induction through the sample coils ranged up to 15% of the amount corresponding to unit permeability, the correction amounted to about 1.6% of the measured values of the susceptibility.

The fluxmeter arrangement used by Giauque, and Stout[2] did not involve coils which were extended, or located entirely, beyond the end of the major axis of the ellipsoid. Thus in the derivation of their equations they did not find it necessary to consider this problem.

Investigation has shown that the equation given by the above authors is generally applicable regardless of the position of the coil so long as it is coaxial with the major axis of the ellipsoid.

The nomenclature of Giauque and Stout will be used in the proof.

Let $2c$ be the length, and $2a$ the diameter, of a prolate ellipsoid.

$$\text{The eccentricity } e = \sqrt{1 - (a^2/c^2)} \qquad (1)$$

$$\text{Let } Q = 4\pi \frac{1 - e^2}{e^3} \mathrm{I} \qquad (2)$$

where I is the intensity of magnetization per cm.^{3} within the ellipsoid and directed along its major axis.

The convenient variable u is defined by the equation

$$\frac{z^2}{u^2} + \frac{r^2}{u^2 - e^2c^2} = 1 \qquad u > ec \qquad (3)$$

where r and z are cylindrical coördinates, the z-axis being taken as coincident with the major axis of the ellipsoid, and the origin of coördinates as the center of the ellipsoid.

H_0 is the magnetic field applied parallel to the major axis of the ellipsoid. As is well known, the field inside the ellipsoid is uniform and directed along the major axis

$$\mathrm{H(inside)} = \mathrm{H}_0 - N\mathrm{I} \qquad (4)$$

where N is the demagnetization factor

$$N = \frac{4\pi(1 - e^2)}{e^2}\left[\frac{1}{2e}\ln\frac{1 + e}{1 - e} - 1\right] \qquad (5)$$

Let G represent the amount of magnetic induction through a turn of a coil of radius b at height z, less the induction through the same coil in the absence of the sample.

Then the average additional induction per turn is

$$\frac{1}{h}\int_0^h G\mathrm{d}z \qquad (6)$$

From equation 17 of Giauque and Stout

$$\frac{1}{h}\int_0^h G\mathrm{d}z = -\pi Q\left[\frac{b^2}{2}\ln\frac{u + ec}{u - ec} - ecu + \frac{h^2ec}{u} - \frac{2}{3}\frac{h^2e^3c^3}{u^3}\right] \qquad (7)$$

which they considered for their experimental case of coils which could extend for any length up to the end of the ellipsoid where $h = c$.

Let us consider the case of a coil which starts at the end of the ellipsoid and extends beyond it to any point h.

$$G = \pi\int_0^{b^2}(\mathrm{H}_z - \mathrm{H}_0)\,\mathrm{d}r^2 = -\pi\int_0^{b^2}\left(\frac{\partial\psi}{\partial z}\right)\mathrm{d}r^2 \qquad (8)$$

$$\text{where } \psi = \left(\frac{Q}{2}\ln\frac{u + ec}{u - ec} - \frac{Qec}{u}\right) z \qquad (9)$$

$$\begin{aligned}\int_c^h G\mathrm{d}z &= -\pi\int_0^{b^2}\int_c^h\left(\frac{\partial\psi}{\partial z}\right)\mathrm{d}z\mathrm{d}r^2 \\ &= -\pi\int_0^{b^2}\psi(h,r)\mathrm{d}r^2 + \pi\int_c^{b^2}\psi(c,r)\mathrm{d}r^2 \\ &= -\pi Q\left[\int_0^{b^2}\left(\frac{h}{2}\ln\frac{u + ec}{u - ec} - \frac{hec}{u}\right)\mathrm{d}r^2 - \right. \\ &\qquad \left.\int_0^{b^2}\frac{c}{2}\ln\frac{u + ec}{u - ec} - \frac{ec^2}{u}\Big)\,\mathrm{d}r^2\right] \qquad (10)\end{aligned}$$

where $u = \mathrm{f}\ (h,r)$ in the first integral and $u = \mathrm{f}\ (c,r)$ in the second.

Integrating by parts and substituting for $\mathrm{d}r^2$ the equation

$$\mathrm{d}r^2 = \left(2u - 2\frac{h^2e^2c^2}{u^3}\right)\mathrm{d}u \qquad (11)$$

$$\begin{gathered}\int_c^h G\mathrm{d}z = -\pi Q\left[\frac{hb^2}{2}\ln\frac{u_{(\mathrm{h,b})}+ec}{u_{(\mathrm{h,b})}-ec} - hec\int_{r=0}^{r=b}\left(1+\frac{h^2}{u^2_{(\mathrm{h})}}-\frac{2h^2e^2c^2}{u^4_{(\mathrm{h})}}\right)\mathrm{d}u - \frac{cb^2}{2}\ln\frac{u_{(\mathrm{o,b})}+ec}{u_{(\mathrm{o,b})}-ec} + ec^2\int_{=0}^{r=b}\left(1+\frac{c^2}{u^2_{(\mathrm{o})}}-\frac{2e^2c^4}{u^4_{(\mathrm{o})}}\right)\mathrm{d}u\right] = \\ -\pi Q\left[\frac{hb^2}{2}\ln\frac{u_{(\mathrm{h,b})}+ec}{u_{(\mathrm{h,b})}-ec} - hec\left(u_{(\mathrm{h,b})}-\frac{h^2}{u_{(\mathrm{h,b})}}+\frac{2h^2e^2c^2}{3u^3_{(\mathrm{h,b})}}\right) - \frac{cb^2}{2}\ln\frac{u_{(\mathrm{o,b})}+ec}{u_{(\mathrm{o,b})}-ec} + ec^2\left(u_{(\mathrm{o,b})}-\frac{c^2}{u_{(\mathrm{o,b})}}+\frac{2e^2c^4}{3u^3_{(\mathrm{c,b})}}\right)\right] \quad (12)\end{gathered}$$

Except for the limits of integration, the expression for the $\int G\mathrm{d}z$ for a coil beyond the end of the ellipsoid is identical with the equation representing the same integral for a coil surrounding the ellipsoid; thus the average additional induction per turn of coil of radius b extending from any h_1 to h_2 is

$$\frac{1}{h_2-h_1}\int_{h_1}^{h^2} G\mathrm{d}z = \frac{4\pi^2}{(h_2-h_1)}\,\frac{(e^2-1)}{e^3}\,\mathrm{I}\left[\frac{hb^2}{2}\ln\frac{u_{(\mathrm{h,b})}+ec}{u_{(\mathrm{h,b})}-ec} - hec\left(u_{(\mathrm{h,b})}-\frac{h^2}{u_{(\mathrm{h,b})}}+\frac{2h^2e^2c^2}{3u^3_{(\mathrm{h,b})}}\right)\right]_{h_1}^{h_2} \quad (13)$$

This is evidently due to the fact that although the arbitrary continuation of the function expressing the magnetic induction outside the ellipsoid, to the space within it, does not represent the actual induction at a given point, the average vertical component of the induction entering the ellipsoid must equal the uniform induction within. Thus equation 10 of Giauque and Stout[2] which is

$$G = \pi\int_{\left(1-\frac{z^2}{c^2}\right)a^2}^{b^2}(\mathrm{H}_z-\mathrm{H}_0)\mathrm{d}r^2 + \pi\int_0^{\left(1-\frac{z^2}{c^2}\right)a^2}(4\pi-N)\mathrm{I}\mathrm{d}r^2$$

may be written and integrated more simply as

$$G = \pi\int^{b^2}(\mathrm{H}_z-\mathrm{H}_0)\mathrm{d}r^2 = -\pi\int_0^{b^2}\left(\frac{\partial\psi}{\partial z}\right)\mathrm{d}r^2 \quad (8)$$

$$\mathrm{I} = \chi\mathrm{H}_{(\mathrm{inside})} \quad (14)$$

Combining this with equation 4

$$\mathrm{I} = \frac{\chi\mathrm{H}_0{}^{7}}{1+\chi N} \quad (15)$$

Let A_0 represent the fluxmeter reading corresponding to unit permeability, $(A_s + A_0)$ the reading when the sample is present and f the value of the coil arbitrarily selected as the unit for the fluxmeter.

$$\text{Then } \frac{1}{\mathrm{H}_0\,(h_2-h_1)}\int_1^{h_2} G\mathrm{d}z = \frac{fAs}{n} \quad (16)$$

where n is the number of turns in the coil. Thus

$$\frac{fAs}{n} = \frac{4\pi^2(e^2-1)\chi}{(h_2-h_1)(1+\chi N)e^3}\left[\frac{hb^2}{2}\ln\frac{u_{\mathrm{h,h}}+ec}{u_{\mathrm{h,b}}-ec} - hec\left(u_{\mathrm{h,b}}-\frac{h^2}{u_{\mathrm{h,b}}}+\frac{2}{3}\,\frac{h^2e^2c^2}{u^3_{\mathrm{h,b}}}\right)\right]_{h_1}^{h_2} \quad (17)$$

Equation 17 applies both to the coils about the sample and to the secondary reference fluxmeter coils.

A first approximation value of the magnetic susceptibility may be obtained without correcting for the effect of the sample on the reference coils and this value will then serve to establish the necessary corrections.

The above equations treat the problem as though the coils all consisted of a single layer of radius b. This of course is not the case as it is desirable to have coils with layers extending over a considerable thickness. Accordingly before using equation 17 it is necessary to sum the contributions made by the several layers of each coil.

As mentioned previously either the solenoid magnet coil or a special exciting coil could be used in fluxmeter measurements. When the solenoid magnet coil was used the factor f = 45.30 ± 0.05 cm.^{2} The exciting coil was wound with a somewhat smaller number of turns per unit length; a value of f = 55.45 ± 0.05 cm.^{2} was used for data obtained with the special exciting coil.

When values were recorded in terms of an autocalibration based on the secondary reference fluxmeter unit coil, a conversion factor had to be applied to convert the values to the primary fluxmeter units. This conversion factor as well as the autocalibration must be checked each time the secondary coils are cooled to the temperature of liquid helium so that the effects of any dimensional changes can be taken into account. In the experiments on cobaltous sulfate heptahydrate[1] mentioned above it was found that one secondary unit equals 0.7908 primary unit.

An example of data obtained in the above work using the secondary reference coils and the specially wound exciting coil is as follows

Fluxmeter reading	=	1509.05	
Correction for effect of sample on reference coils	=	3.05	
Corrected reading	=	1512.10	
Coil value at unit permeability	=	1334.87	
Net effect	=	177.23	secondary units
A_s	=	140.15	primary units

χ vol. = 0.0392

The ellipsoid contained 0.1627 mole in its volume of 38.42 cm.^{3}.

$$\text{Thus } \chi \text{ molal} = \frac{0.0392 \times 38.42}{0.1627} = 9.26$$

The calculation above and equations 15 and 17 are for the initial magnetic susceptibility. The expression $\mathrm{I} = \chi\mathrm{H}_{(\mathrm{inside})}$ holds by definition for the isothermal magnetic susceptibility in any field. However, a fluxmeter of the type described here could not correctly determine an isothermal change in the intensity of magnetization for a large change in field. In this case the magnetic material would be unable to dispose of the heat developed during magnetization with sufficient rapidity to maintain the isothermal condition.

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(7) In the paper of Giauque and Stout the χ was omitted from the numerator of this equation (their equation 19) and π was omitted from the first term following the equal sign in their equation 10. These typographical errors caused no other errors.

However equation 13 is of outstanding importance in large fields in connection with the determination of the reversible adiabatic, or isentropic, magnetic susceptibility.

The Calculation of the Isentropic Magnetic Susceptibility.—The thermodynamic properties of a substance in a magnetic field are a function of its shape as well as its interior constitution. If the thermodynamic treatment is to be combined or compared with the quantum statistical properties of the substance it is desirable to apply the demagnetization factor in obtaining the interior field, which has been called $\mathbf{H}_{(\text{inside})}$ above, since this is the net field which controls the distribution among the several quantum states of the system.

However, one can express the various thermodynamic relationships in terms of the applied field if it is desired to do so. In this latter case the body may have any irregular shape; however, the use of any shape other than an ellipsoid imposes certain experimental restrictions. For example, a body of some other shape subjected to a considerable change in magnetic field will produce different amounts of heat per unit volume in different portions of the material. Thus a reversible magnetization would have to be performed slowly enough so that any heat developed could be completely distributed. Such a process would be too slow to permit the most accurate use of a fluxmeter such as that described here. An even greater objection to a sample of some shape other than an ellipsoid is connected with the great difficulty in knowing the distribution of the magnetic induction produced by the external field. From a strictly thermodynamic point of view it would not be necessary to know this distribution but only the total work done in magnetizing the body. While such data may be of interest in the design of equipment it is not very suitable for advancing our knowledge of the actions and interactions of the magneton units within the substance. In the case of ellipsoidal shapes the intensity of magnetization and thus the production of heat is the same at all points. If the sample is thermally isolated and enclosed in a container of negligible heat capacity and the magnetic interactions are fairly rapid, the system is ideal for the application of the above equations for small variations in large fields. In this case the changes take place at constant entropy. If the container has an appreciable heat capacity, the differential susceptibilities will be essentially isentropic, but the entropy of the substance will vary with the total field.

Consider a case where a large field is increased by steps and differential measurements are to be made by very small variations of the fluxmeter field at each step. The substance and its container are thermally isolated but the container has heat capacity. If the magnetic field is increased suddenly by one step the substance will heat up. This will be followed by the irreversible flow of heat to the container with a small increase in entropy. Fortunately it is possible to use containers which have a negligible heat capacity at the temperatures of liquid helium and it is possible to determine either of the quantities

$$(\partial \mathrm{I}/\partial \mathrm{H}_0)_{\mathrm{S}} \text{ or } (\partial \mathrm{I}/\partial \mathrm{H})_{(\text{inside})\mathrm{S}}$$

with considerable accuracy. S represents the entropy of the substance. The quantity

$$\frac{1}{h_2 - h_1}\int_{h_1}^{h_2} G\mathrm{d}z = \frac{fAs\mathrm{H}_0}{n} \qquad (18)$$

is the magnetic induction cutting an average turn of the coil due to the presence of the sample in the applied field $\mathbf{H}_0$. Also

$$\frac{fAs\mathrm{H}_0}{n} = \text{const. (1)} \times \mathrm{I} \qquad (19)$$

where the constant is given by equation 17

$$\text{const. (1)} = \frac{4\pi^2(e^2 - 1)}{(h_2 - h_1)e^3}\left[\frac{hb^2}{2}\ln\frac{u_{(\mathrm{h,b})} + ec}{u_{(\mathrm{h,b})} - ec} - hec \left(u_{(\mathrm{h,b})} - \frac{h^2}{u_{(\mathrm{h,b})}} + \frac{2}{3}\,\frac{h^2e^2c^2}{u^3_{(\mathrm{h,b})}}\right)\right]_{h_1}^{h_2} \qquad (20)$$

$$\left(\frac{\partial \mathrm{I}}{\partial \mathrm{H}_0}\right)_{\mathrm{S}} = \frac{f}{n \times \text{const. (1)}}\left(\frac{\partial As\mathrm{H}_0}{\partial \mathrm{H}_0}\right)_{\mathrm{S}} \qquad (21)$$

When the sample is magnetized in a large field $\mathbf{H}_0$, the increment of magnetic induction, per average turn, balanced by the fluxmeter when the exciting coil changes $\mathbf{H}_0$ by $\mathrm{d}\mathbf{H}_0$ is $[f/n\ \text{const.}(1)]$ $\mathrm{d}(As\mathbf{H}_0)$ per unit volume of the magnetic substance. Thus the quantity $(\partial \mathbf{I}–\partial \mathbf{H}_0)_{\mathrm{s}}$ is directly measured. The quantity $(\partial \mathrm{I}/\partial \mathbf{H}_{(\text{inside})})\mathrm{s}$ may be calculated from the relation

$$\mathrm{H}_{(\text{inside})} = \mathrm{H}_0 - N\mathrm{I} \qquad (5)$$

$$\left(\frac{\partial \mathrm{H}_{(\text{inside})}}{\partial \mathrm{I}}\right)_{\mathrm{S}} = \left(\frac{\partial \mathrm{H}_0}{\partial \mathrm{I}}\right)_{\mathrm{S}} - N \qquad (22)$$

from which

$$\left(\frac{\partial \mathrm{I}}{\partial \mathrm{H}_{(\text{inside})}}\right)_{\mathrm{S}} = \frac{(\partial \mathbf{I}/\partial \mathbf{H}_0)_{\mathrm{S}}}{1 - N\left(\frac{\partial \mathrm{I}}{\partial \mathrm{H}_0}\right)_{\mathrm{S}}} \qquad (23)$$

This is entirely equivalent to equation 17 in which the symbol χ can be replaced by $(\partial \mathbf{I}/\partial \mathbf{H}_{(\text{inside})})\mathrm{s}$ for the initial susceptibility.

It is much more important to observe such differential rather than total quantities since they permit the evaluation[8] of such quantities as changes of energy, heat content, thermodynamic temperature or the isothermal intensity of magnetization as a function of field.

The Fluxmeter as a Test for Reversibility.—If a magnetic system has appreciable hysteresis it would not be possible to obtain a good balance on a sensitive fluxmeter of this type. The lag in the building up or the decay of the intensity of magnetization would cause a delayed galvanometer deflection which cannot be balanced by the e. m. f. from the fluxmeter coils at essentially unit permeability. A conceivable case is one where a

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(8) Giauque and MacDougall, THIS JOURNAL, **57**, 1175 (1935); **60**, 376 (1938).

portion of the system has hysteresis which is so slow that a spurious balance is obtained. In the study of paramagnetic systems at low temperatures the onset of coöperative phenomena, such as ferromagnetism, should be rather gradual. For this reason, it seems unlikely that such severe hysteresis as that mentioned above could develop without observable effects due to its initial stages.

Summary

A fluxmeter for measuring the reversible adiabatic magnetic susceptibility in the presence of large fields has been devised and tested.

Equations relating the observed magnetic induction to the susceptibility of the sample have been given.

Cadmium–zinc solder has been suggested for use in magnetic apparatus at the temperature of liquid helium where the superconductive properties of ordinary solder are objectionable if sensitive measurements are desired.

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[CONTRIBUTION FROM THE DEPARTMENT OF SANITARY ENGINEERING, GRADUATE SCHOOL OF ENGINEERING, HARVARD UNIVERSITY]

Kinetic Studies on the Chloramines. I. The Rates of Formation of Monochloramine, N-Chlormethylamine and N-Chlordimethylamine[1]

BY IRA WEIL AND J. CARRELL MORRIS

In aqueous solution, chlorine or hypochlorites react readily with ammonia or ammonium ions to give a series of products—monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and nitrogen trichloride (NCl_3).[2] Presumably these products are formed successively so that the reactions that occur may be represented stoichiometrically by the equations

$$HOCl + NH_3 \longrightarrow NH_2Cl + H_2O \quad (1)$$

$$HOCl + NH_2Cl \longrightarrow NHCl_2 + H_2O \quad (2)$$

$$HOCl + NHCl_2 \longrightarrow NCl_3 + H_2O \quad (3)$$

These reactions are of great practical importance in the disinfection of water supplies with chlorine or hypochlorites and in addition, as will be shown, are of considerable interest from the viewpoint of theoretical solution kinetics. Hence, a detailed study of their rates has been undertaken.

The present paper deals principally with the first of these reactions—the rate of formation of monochloramine. The rates of similar reactions of aqueous chlorine with methylamine and dimethylamine or their salts have also been studied to aid in the interpretation of the results obtained with ammonia.

The interaction of aqueous chlorine and ammonia or amines is so rapid that the rate is measurable by ordinary techniques only at very low concentrations of the order of $10^{-5}M$. At such dilutions, provided large concentrations of H^+ or Cl^- are not present, the hydrolysis of chlorine to hypochlorous acid is virtually complete (better than 99.99% in all the experiments). Hence, it is presumably HOCl or OCl^- which takes part in the reactions—as shown by the equations. This conclusion is substantiated by the data presented later.

The progress of the reactions was generally followed by measuring colorimetrically the decrease in the concentration of unreacted $HOCl + OCl^-$ with time. This gives the rate of formation of monochloramine if reactions (2) and (3) do not occur simultaneously. In order to minimize the interference by these succeeding reactions, all of the experiments were carried out in the presence of a considerable excess of ammonia or ammonium ions, and determinations of the rate were based primarily on results for the initial period of the reaction.

As a check on the sufficiency of these precautions some experiments were conducted by a different technique. It was possible, under certain conditions, to follow the reaction spectrophotometrically, using the increasing intensity of the NH_2Cl band at 245 mμ[3,4] as a direct measure of its rate of formation. The two methods gave results in good agreement.

The rate of reaction of aqueous chlorine with dimethylamine provided another check that the measured rates of disappearance of hypochlorite were equal to the rates of formation of monochloramine. With dimethylamine only a monochloro derivative results, its formation corresponding to the reaction

$$(CH_3)_2NH + HOCl \longrightarrow (CH_3)_2NCl + H_2O \quad (4)$$

Parallel results were obtained for the reactions of aqueous chlorine with ammonia and with dimethylamine, a fact which gives added assurance that the observed rates for the ammonia reaction are to be attributed to reaction (1).

Experimental

Reagents.—For experiments with very low concentrations of chlorine it is essential that the reaction medium (distilled water or salt solution) be free of all traces of

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[1] This paper is based on work performed under Contract No. W-44-009 eng-463 for the Engineer Research and Development Laboratories, U. S. Army.

[2] See Berliner, *J. Am. Water Works Assoc.*, **23**, 1320 (1931), for a review of the chemistry of these compounds.

[3] Metcalf, *J. Chem. Soc.*, 148 (1942).

[4] Burden, Doctoral Thesis, 1948, Graduate School of Engineering, Harvard University.