measurements the entropy was fixed in terms of initial susceptibility measurements.

The above measurements were combined to permit the first determination of thermodynamic temperatures in the region made available by the magnetic cooling method. Our preliminary reports on this subject were based on the data which are presented here. It is found that the thermodynamic scale agrees with the temperatures predicted by Curie's law for gadolinium phosphomolybdate down to 0.15°K.

The temperature change during adiabatic magnetization has been tabulated.

The energy change during isothermal magnetization at 1.4°K. has been shown to be practically zero, as would be expected for an ideal paramagnetic substance.

BERKELEY, CALIF. RECEIVED OCTOBER 29, 1937

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

Induction Heaters for Calorimetry below 1°K. An Investigation of the Electrical Resistance of Gold-Silver Alloys at Low Temperatures

BY W. F. GIAUQUE AND J. W. STOUT

In a previous paper it has been shown experimentally by Giauque and MacDougall[1] that induction heaters are well adapted to calorimetry below 1°K. The advantage of this type over the ordinary kind of electrical heater is the absence of direct electrical connections to contribute to calorimetric heat leak. In order to obtain a sense of proportion about the small amounts of energy concerned in calorimetry at these temperatures we will recall some of the values in the experiments on gadolinium phosphomolybdate.[1]

Although the 63-cc. calorimeter contained an 89-g. sample, the total energy change between 0 and 1°K. was only 0.03 cal. In order to investigate the rapidly varying form of the heat capacity curve below 1°K., it was necessary to add about 0.001 cal. for an individual experiment. In the previous work, this increment of energy was measured with an accuracy of the order of 10^{-5} cal. We saw no reason why this accuracy of energy measurement could not be increased easily to at least one millionth of a calorie or 0.1% if a suitable heater material could be found. The search for such a material is the subject of this paper.

In selecting a heater material it is expedient to avoid conductors that become superconducting, although such conductors conceivably could be used in a method that effected a temporary restoration of resistance. For example the application of a sufficient magnetic field could restore the resistance until the local rise in temperature of the heater was able to maintain it. The material should not be appreciably para or ferromagnetic. It is convenient to construct a heater of a substance that is chemically unreactive. When energy is being developed, the heater material will vary in temperature in some unknown manner depending on the rate of heat input and the rate at which the heat can be transferred to the sample. This makes it necessary that the electrical resistance of the material should be sufficiently constant over the possible range of temperatures that can exist during energy input. The greatest uncertainty at present is connected with what may happen to electrical conductivity below 1°K. Fortunately the heat capacity of most materials in this region is so small that the heater would be removed from this temperature region by the first, and a negligible, portion of the energy developed. To determine the temperature range over which the electrical resistance must remain constant a safe criterion would be to calculate the temperature that would be attained if all the energy introduced were retained by the heater.

A rapid survey of the available data made it clear that no pure element could meet the above requirements. Even without excluding magnetic materials and numerous superconducting substances the resistance of pure metals is not sufficiently constant. It is impracticable to design pure metal heaters of desirable form and at the same time having a proper ratio of heat capacity to energy developed in order to limit the possible temperature range during operation. It might be pointed out that this ratio can be varied by changing the value of the alternating magnetic field used for inducing the eddy currents. However, small alternating fields are often used to make magnetic susceptibility measurements by the induction method and it is desirable to have a heater that will not liberate an appreciable amount of energy unless larger fields are used. To minimize further the above effect it seems desirable that the heater should be located at some distance from the sample and measuring coil, although some means must be provided for thermal contact. Another reason for placing the heater at some distance from the magnetic sample is that the presence of magnetic material will distort the alternating field and necessitate a correction that will depend, often not in a simple manner, on the varying permeability of the sample.

Consideration of Metallic Alloys.—In general an alloy of two or more metallic elements has a much lower electrical

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[1] Giauque and MacDougall, THIS JOURNAL, **60**, 376 (1938).

conductivity than the constituent metals. Moreover, the temperature coefficient of conductivity of such an alloy is characteristically much lower than that of pure metals. In well-known cases such as constantan and manganin[2] there is little temperature coefficient of resistance near ordinary temperatures or even to temperatures near 100°K. However, we have mentioned these cases particularly because they demonstrate that such behavior at higher temperatures is not a very safe guide to the nature of the changes to be expected in the liquid helium–liquid hydrogen temperature range. Each of these alloys, even if it could meet other requirements, changes so rapidly in electrical resistance in this temperature region as to be useless for our purpose.

For many years most of the low temperature calorimetry in this Laboratory has been carried out with the assistance of gold resistance thermometer-heaters. While pure gold is a very satisfactory metal for resistance thermometer purposes above the temperatures of liquid hydrogen, its resistance drops to such a low value that it is undesirable for an electrical heater. For this reason Giauque and Wiebe[3] constructed a thermometer-heater of gold to which 0.175% silver had been added since Kamerlingh Onnes and Clay[4] had found that the presence of small amounts of silver prevented the resistance of the alloy from falling to very small values at the temperatures of liquid hydrogen. The experience of workers in this Laboratory with many such gold thermometer-heaters having silver contents of 0.1–0.2% had shown that they lost nearly all temperature coefficient of resistance near 10°K. and of course became useless for thermometric purposes. The investigations had not been extended to the temperatures of liquid helium.

When Giauque and MacDougall[1] considered the problem of selecting a suitable material for use as an induction heater, experimental expediency led to the selection of some of the readily available thermometer-heater wire containing about 0.1% silver. While this alloy served well in the preliminary experiments its characteristics are still too much like those of a pure metal to permit the very high accuracy we now hope to attain. A search of the literature showed that the electrical resistance of the gold–silver alloy system has been investigated extensively[5–9] at temperatures above 85°K. and that the specific electrical resistance is relatively large for all alloys having considerable amounts of both silver and gold.

Clay[4b] has extended the investigation of this system to the temperatures of liquid hydrogen. The above results indicated that gold–silver alloys might meet our requirements so we decided to investigate this system at the temperatures of liquid helium. Also a few measurements were made at higher temperatures since this could easily be done once the apparatus was set up.

The perfection of the solid solutions formed by gold and silver, and the fact that these metals do not have crystalline transformations which might impede the attainment of equilibrium in the alloys, were important factors in favor of this choice.

The Electrical Resistance of Gold–Silver Alloys.—Five gold–silver alloys containing from 10 to 90 atomic per cent. of silver were drawn into wires 0.0579 cm. in diameter and roughly 100 cm. in length. A similar wire of copper containing 1 atomic per cent. of silver was made. An alloy containing 50 atomic per cent. of copper and silver was too hard to be drawn conveniently so it was not included. All of the above alloys were annealed by heating to redness in a flame during and after the drawing. The wires were wound loosely on a spool in insulated layers and were then annealed for about fifteen hours at 110°. In addition to the above alloys a sample of the wire used by Giauque and MacDougall[1] was included. It was investigated without removal from the spool from which their sample had been taken. This wire had been insulated with a double layer of silk and had been annealed before the insulation was applied. It was not annealed further before the present measurements, a fact which will be of interest later. The data relating to the composition and specific resistance of the several alloys are given in Table I.

Table I

Composition of Gold–Silver and Copper–Silver Alloys and their Specific Resistance at 0°C.

Atomic weights: Au = 197.2, Ag = 107.880, Cu = 63.57

No.	Type	Wt. % Ag	Atom % Ag	Resistance of sample at 0°C. ohms	Specific resistance microhm cm. at 0°C.
1	Au–Ag	83.12	89.99	0.19864	5.06
2	Au–Ag	56.08	69.98	.44902	9.48
3	Au–Ag	35.33	49.90	.42483	10.96
4	Au–Ag	18.99	29.98	.39991	9.10
5	Au–Ag	5.73	9.99	.24314	4.87
6	Au–Ag	0.1	0.2	14.0568	2.44
7	Cu–Ag	1.68	1.00	0.08280	1.76

The measurements of specific resistance were made at a temperature of 25°C. and corrected to 0°C. by means of the resistance–temperature data to be given later. The correction for thermal expansion amounts to only a few hundredths of one per cent. and did not change the values of specific resistance within our limit of accuracy for this quantity. Since we were not particularly concerned with accurate specific resistance data, the measurements may be in error by nearly a per cent. However, the resistance of various samples relative to their ice-point values was made with an accuracy of about one part in ten thousand in most cases.

The samples were mounted a short distance above a motor driven stirrer in a dewar of about eight-liter capacity. The dewar was arranged so that liquid helium, liquid hydrogen, liquid air or solid carbon dioxide could be introduced. All liquid baths were stirred thoroughly. The lower temperatures were measured with a vapor pressure thermometer mounted with the samples. The thermometer was filled with helium or hydrogen as circumstances required. Temperatures of the liquid air and

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(2) Kamerlingh Onnes and Holst, *Comm. Phys. Lab. Univ. Leiden*, No. 142A.

(3) Giauque and Wiebe, This Journal, **50**, 101 (1928).

(4) (a) Kamerlingh Onnes and Clay, *Comm. Phys. Lab. Univ. Leiden*, No. 99c, 1907; (b) Clay, *ibid.*, No. 107d.

(5) Matthiessen, *Ann. phys. Chem. (Poggendorf)*, **186**, 190 (1860).

(6) Matthiessen and van Bose, *ibid.*, **191**, 353 (1862).

(7) Matthiessen and Vogt, *ibid.*, **198**, 19 (1864).

(8) Fleming, *Proc. Roy. Inst.*, **15**, 239 (1896).

(9) Beckman, Thesis, Upsala (1911); see "I. C. T.," Vol. VI, p. 160.

TABLE II

$R_T/R_{273.1°K.}$ FOR GOLD-SILVER AND COPPER-SILVER ALLOYS AT LOW TEMPERATURES

Run no.	Date	T, °K.	Alloy: 1	2	3	4	5	6	7
21	1/23/37	1.6	0.6720	0.8098	0.8220	0.7776	0.5724	0.099000	0.0900
24	5/10/37	1.63	.6715	.8095	.8222	.7774	.5719	.098693*	.0896
11	11/22/34	1.98	.6723	.8094	.8219	.7774	.5722	.098586	.0903
9	11/28/34	4.23	.6726	.8094	.8220	.7774	.5723	.096871	.0905
10	11/29/34	4.24	.6719	.8094	.8220	.7772	.5725	.096866	.0912
20	1/23/37	4.23	.6714	.8096	.8220	.7773	.5723	.096834	.0891
22	5/10/37	4.23	.6715	.8095	.8221	.7772	.5718	.096545*	.0897
23	5/10/37	4.23	.6716	.8095	.8221	.7772	.5718	.096544*	.0896
6	11/21/34	12.0	.6729	.8099	.8225	.7778	.5730	.096270	.0912
7	11/21/34	12.0	.6731	.8098	.8224	.7777	.5729	.096277	.0909
4	11/21/34	13.92	.6733	.8100	.8226	.7780	.5735	.097038	.0911
5	11/21/34	13.92	.6732	.8100	.8225	.7780	.5734	.097031	.0906
2	11/21/34	20.44	.6753	.8112	.8239	.7798	.5770	.103573	.0918
3	11/21/34	20.44	.6751	.8114	.8239	.7798	.5770	.103558	.0920
8	11/24/34	20.45	.6750	.8111	.8239	.7798	.5772	.103590	.0913
14	12/1/34	59.17	.7159	.8357	.8475	.8103	.6377	.22386	.1570
12	12/1/34	81.36	.7473	.8539	.8643	.8315	.6782	.30891	.2370
13	12/1/34	81.37	.7475	.8537	.8643	.8315	.6785	.30896	.2370
15	12/3/34	194.62	.8999	.9409	.9457	.9321	.8711	.71969	.6961
18–19	4/9/35	273.10	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
16	12/15/34	293.57	1.0266	1.0156	1.0143	1.0154	1.0339	1.07473	1.0790
1	11/19/34	296.2	1.0303	1.0174	1.0162	1.0209	1.0380	1.08074	1.0886
17	4/9/35	298.36	1.0324	1.0190	1.0176	1.0220	1.0420	1.09064	1.0978

carbon dioxide baths were obtained with a thermocouple. The carbon dioxide was allowed to come to equilibrium with the pressure of the atmosphere. The data at 0°C. and above were obtained in a separate dewar. A kerosene filled sample tube was immersed in an ice-bath for the measurements at 273.10°K. The temperatures above the ice-point were measured with a mercury thermometer reading to 0.002° and calibrated by the Bureau of Standards. Liquid helium, liquid hydrogen and liquid air were prepared in laboratory liquefiers and transferred to the apparatus. Solid carbon dioxide snow was obtained by forcing a stream of carbon dioxide gas into the liquid air filled dewar. The temperature measurement at 12.0°K. was not very reliable but this is not very important as the change of resistance with temperature is so small in that region. The resistances were measured by a potentiometer method and the arrangement was such as to give a somewhat greater accuracy with coil No. 6 than with coils 1–5 inclusive. Coil 7 had a decidedly poorer accuracy than the 0.01–0.02% obtained with coils 1–5 because the sample not only had a small resistance at the ice-point but it decreased rapidly with temperature. Small thermoelectric effects were found in the various circuits and it was necessary to measure and correct for these in order to attain an accuracy of 0.01–0.02%. The data are presented in Table II. The values at the ice-point were measured on two occasions and averaged. The individual measurements agreed to one part in ten thousand or better except in the case of sample No. 7 where the value was determined to ±0.02%. To test the effects of successive coolings and of time on the resistance of the alloys the samples were cooled to the temperatures of liquid helium on four occasions over a period of two and one-half years. Following Run No. 7 the apparatus was warmed to room temperature and measurement No. 8 was made three days later. The agreement of Run No. 8 with Runs No. 2 and 3 after the recooling is very satisfactory, especially when it is considered that the sample coils were not wound entirely strain free. The apparatus was again warmed after Run No. 8 and four days later measurements were resumed.

The agreement at the temperatures of liquid helium after the samples had been mounted in a new apparatus and measured over two years later is especially satisfactory. Before the last measurements, listed as Runs No. 22, 23 and 24 on 5/10/37, an accident caused the alloys to be heated to a temperature a little over 100° for about six or eight hours. Some differences in the measurements obtained in these runs are attributable to this cause, especially in the case of alloy No. 6. These values have been marked with an asterisk. As mentioned above, this particular sample had not been re-annealed after being insulated and wound on a spool. After Runs 22, 23 and 24, the room temperature resistance of alloy No. 6 was found to be in agreement with the original value. This is consistent with the usual effects of annealing. For example, the resistance of ordinary copper wire at temperatures below 20°K. can be reduced to one-half of its original value by annealing at 100°C. for a few hours, although the room temperature resistance is not altered appreciably.

For the measurements of 1/23/37 and 5/10/37 the samples were cooled to the temperature of liquid helium in a dewar enclosed by a solenoid magnet. We had not originally intended to investigate the effect of a magnetic field on the alloys, so the coils had not been wound non-inductively. This led to some loss in accuracy; however, by means of a compensating coil most of the induction effects caused by irregularities in the magnet current were balanced out. The magnetic field was directed along the axis of the coils. The effect of the maximum field, 8400 gauss, on the resistance of most of the alloys was so small that only the order of magnitude can be given. At both 4.23 and 1.63°K. the resistance for alloys No. 2, 3 and 4 increased by about 2 parts in 100,000 in a field of 8400 gauss. Alloys No. 1 and 5 increased by about 5 parts in 100,000 and alloy No. 7 increased by about three parts in 1000 under the same conditions. Alloy No. 6 showed a considerable change and the results seemed sufficiently interesting to justify closer study. The data, some of which were presented previously,[10] are given in Table III. The annealing, mentioned above, before the run of 5/10/37, produced little effect.

TABLE III

CHANGE OF RESISTANCE OF GOLD, CONTAINING 0.1% SILVER, WITH A MAGNETIC FIELD

Date, 1/23/37. $T = 4.23$°K.

$\mathbf{H}_{\text{gauss}}$	3270	3350	6070	6210	8360	8490
$\Delta \mathbf{R} \times 10^4/\mathbf{R}$	6.3	6.5	15.7	16.0	25.5	26.0

Date, 5/10/37. $T = 4.23$°K.

$\mathbf{H}_{\text{gauss}}$	1630	2450	3230	6040	8490
$\Delta \mathbf{R} \times 10^4/\mathbf{R}$	2.8	4.8	6.4	15.7	26.8

Date, 5/10/37. $T = 1.63$°K.

$\mathbf{H}_{\text{gauss}}$	1630	2450	3300	6110	8490
$\Delta \mathbf{R} \times 10^4/\mathbf{R}$	−5.1	−10.5	−18.7	−62.2	−112.3

The decrease in electrical resistance with increasing magnetic field at 1.63°K. is of especial interest. A negative magnetic coefficient of resistance has been observed previously only in the case of ferromagnetic metals and has been ascribed to effects related to ferromagnetism. It may be noticed in Table II that the resistance of alloy No. 6 passes through a minimum, probably about 8°K. At 1.6°K. the resistance is over 2% greater than at 4°K. This effect recently has been observed in very pure gold and silver by de Haas, de Boer and van den Berg.[11] We observed no indication of such an effect in alloys containing considerable amounts of both gold and silver.

The reversal in sign of the magnetic coefficient of resistance between the temperatures 4.23 and 1.63°K. presumably is related to the minimum in the electrical resistance. This magnetic anomaly will be investigated in more detail.

The minimum in the resistance of alloy No. 6, used in the induction heater of Giauque and MacDougall[1] may have caused a small uncertainty in their calorimetric results but this is well within the limit of accuracy of their preliminary measurements.

From the data in Table II it may be seen that any gold–silver alloy containing considerable amounts of each of these elements would be very satisfactory for induction heaters. The data indicate that the 50–50 atomic per cent. alloy is the best for our purpose. If the operating temperature of the heater is limited to the region between 1.6 and 12°K., the uncertainty in the energy would not exceed 0.03%. The effect of a magnetic field is negligible.

The Induction Heater.—An induction heater could be designed to liberate a calculated amount of heat in an alternating field of known intensity. This would require that the dimensions of a given heater be known accurately at the temperatures of liquid helium. Moreover, it would mean that the characteristics of the exciting field should be known with very high accuracy. These difficulties are not present if the heater is calibrated by comparison with an electrical heater of the ordinary type at temperatures above 1°K. This method requires only the accurate measurement of current in the exciting field circuit, the energy developed in unit time being proportional to the square of the current. In using an absolute method the heater shape would be limited to certain simple types whose geometry facilitates an accurate solution of the eddy current problem. In the reference method heaters of any desirable shape may be used and the problem of design becomes a simple one involving only the right orders of magnitude.

The following formulas give the heat developed in several simple cases. It may be shown readily that the impedance is very closely equal to the resistance in the several circuits at a frequency of 60 cycles/sec. and with materials of the specific resistances of gold–silver alloys 1–5. This would not be true with pure metals whose specific resistances decrease to small values at low temperatures:

Case 1: a spherical shell of inside radius a and outside radius b:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{2\pi \times 10^{-16}}{15\rho}(b^5 - a^5)\left(\frac{\mathrm{d}\mathbf{H}}{\mathrm{d}t}\right)^2 \text{ joules/sec.} \quad (1)$$

where t = time in sec., ρ = specific resistance in ohm cm., $\mathbf{H}$ = magnetic field in gauss and q = heat developed in joules. $\mathrm{d}\mathbf{H}/\mathrm{d}t$ may be replaced by the expression $2\pi f \mathbf{H}_{\text{av.}}$ where f is the frequency in cycles/sec. and $\mathbf{H}_{\text{av.}}$ is the root mean square value of the magnetic field.

Case 2: a hollow cylinder of length l, inside radius a, and outside radius b. The magnetic field is directed along the axis.

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(10) Giauque, Stout and Clark, *Phys. Rev.*, **51**, 1108 (1937).

(11) (a) De Haas, de Boer and van den Berg, *Physica*, **1**, 1115 (1934); (b) de Haas and van den Berg, *ibid.*, **3**, 440 (1936).

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{\pi \times 10^{-16}\, l}{8\rho}\,(b^4 - a^4)\left(\frac{\mathrm{d}\mathbf{H}}{\mathrm{d}t}\right)^2 \text{ joules/sec.} \qquad (2)$$

Case 3: a circular ring of circular cross section. a is the distance between the centers of circle and conductor and b is the radius of the conductor. The magnetic field is directed perpendicular to the plane of the ring.

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{\pi^2 \times 10^{-16}}{2\rho}\,(a^3b^2 + 3ab^4/4)\left(\frac{\mathrm{d}\mathbf{H}}{\mathrm{d}t}\right)^2 \text{ joules/sec.} \qquad (3)$$

Spherical heaters have the advantage that they are always symmetrical with respect to the field direction. As an example we will calculate the heat developed by a root mean square average field of 100 gauss acting on a solid sphere 1 cm. in diameter. The material is gold–silver alloy of equal atomic proportions.

From Tables I and II the specific resistance at 0°C. is 10.96×10^{-6} ohm cm. and $R_{4°\mathrm{K.}}/R_{273.1°\mathrm{K.}} = 0.8220$. Therefore neglecting the thermal contraction of volume the specific resistance at 4°K. is approximately $10.96 \times 10^{-6} \times 0.8220 = 9.0 \times 10^{-6}$ ohm cm.

Then from Formula 1

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{2\pi \times 10^{-16} \times 0.5^5 \times (2\pi\, 60 \times 100)^2}{15 \times 9.0 \times 10^{-6}} = 2.1 \times 10^{-4} \text{ joules/sec.} = 3.0 \times 10^{-3} \text{ cal./min.}$$

The above sphere contains 0.026 gram atom of silver and the same of gold. Neglecting small electronic heat capacity effects we may estimate with sufficient accuracy for our present purpose, the energy, $E = 2 \times 10^{-4}T^4$ calories for one "mole" of the alloy.

Therefore $E_{\text{sphere}} = 1 \times 10^{-5}T^4$ cal. If all the heat, 3.0×10^{-3} cal., developed in one minute stayed in the heater its temperature would be 4.2°K. The 3.0×10^{-2} cal. developed in ten minutes would, if none were transferred to the sample, raise the heater temperature to 7.4°K.

It is evident that the maximum possible temperature to which the heater would rise is insufficient to cause an uncertainty in its resistance, and consequently in its rate of developing heat, of more than 0.03%.

It may be shown that the heater would not remain at a very low temperature since the heat developed in one second, under the above conditions, is sufficient to heat it to 1.5°K.

It is evident that the maximum and minimum temperatures at which the heater would operate would not cause an uncertainty in its resistance, and consequently in its rate of developing heat, of more than 0.03%.

We are indebted to Dr. C. W. Clark for assistance with some of the measurements.

Summary

Induction heaters are useful for calorimetry below 1°K. because absence of direct electrical connections eliminates heat leak.

A discussion of the design and construction materials suitable for such heaters has been given.

Measurements of the resistance of six gold–silver alloys and one copper–silver alloy have been made from 2 to 298°K. and the data have been presented in tables.

Any gold–silver alloy with considerable amounts of each constituent is suitable as a material for low temperature induction heaters since the resistance of these alloys changes very little in the temperature range 1.6–12°K.

With an alloy of equal atomic proportions the uncertainty in the energy, due to variation of electric resistance with temperature, would not exceed 0.03%.

Formulas for the heat developed by spherical, cylindrical and ring types of heaters are given. A sample calculation of the heat developed and of the limiting temperatures in a spherical heater is presented.

In a gold alloy containing 0.1%, by weight, of silver, the electrical resistance passed through a minimum at about 8°K. This effect is in agreement with recent similar observations of de Haas, de Boer and van den Berg on very pure gold and silver. No indication of such an effect was observed in gold alloys containing considerable amounts of silver.

At 1.63 and 4.23°K. the resistance of gold alloys containing 10 and 90 atomic per cent. of silver increased by about 5 parts in 10^5 in a magnetic field of 8400 gauss. Alloys containing 30, 50 and 70 atomic per cent. increased by about 2 parts in 10^5 for the same field.

It is evident that gold–silver induction heaters could be used in the presence of large magnetic fields without appreciable correction.

The gold alloy containing 0.1% of silver was investigated in several magnetic fields up to 8490 gauss at 1.63 and 4.23°K. At the upper temperature the magnetic coefficient was positive.

At the lower temperature the resistance decreased by over a per cent. in a field of 8490 gauss. A negative magnetic coefficient of resistance has been observed previously only in the case of ferromagnetic metals.

BERKELEY, CALIF. RECEIVED OCTOBER 29, 1937

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

An Experiment on the Adsorption of Helium Gas Used for Thermal Conduction in Calorimetry near 1°K. The Heat of Adsorption

BY J. W. STOUT AND W. F. GIAUQUE

In the course of their adiabatic demagnetization experiments, Giauque and MacDougall[1] determined the order of magnitude of the amount of helium gas which should be added to a calorimeter to ensure the best possible gas conduction without introducing undesirable heat effects caused by the helium. The principal heat effect is due to the condensation of helium rather than to the heat capacity of gas. The present experiment was not intended to yield very precise or extensive results but rather to help provide a better sense of proportion as to adsorption phenomena occurring in a calorimeter at these temperatures.

Most of the substances which have proved of interest in the adiabatic demagnetization experiments are hydrated salts and the presence of some excess water is ordinarily not objectionable. Thus a typical situation is a calorimeter filled with moist crystals and the adsorption phenomena may well be characteristic of ice rather than of the substance investigated. Although nickel sulfate heptahydrate is not suitable for producing temperatures below 1°K., we happened, in connection with another investigation, to have a convenient opportunity of investigating the adsorption of helium in a sample tube filled with moist crystals of this material. As it appears probable that the results are typical, it seems desirable to present them here.

Seventy-eight grams of $NiSO_4 \cdot 7H_2O$ was broken up until it would pass through a screen with holes 0.5 mm. square. This procedure was to prepare the crystals for other experiments to be reported elsewhere. The crystals were then placed in a saturated solution of nickel sulfate and allowed to stand for three hours to eliminate rough surfaces from the broken crystals. They were then removed from the solution and dried until there was about 0.2 mole of excess water per mole of $NiSO_4 \cdot 7H_2O$. An examination of the crystals under a microscope showed that the average diameter was about 0.25 mm. The crystals were placed in a 62.7-cc. Pyrex glass sample tube which was connected to a McLeod gage measuring system and could be immersed in a liquid helium bath. A known amount of helium gas was added to the sample tube system and line volumes and their temperatures were known with sufficient accuracy to permit calculation of the amount of adsorbed helium at any time.

The experiment was performed in a Dewar flask of about eight liters capacity which was nearly full of liquid helium. As the chronological order in the experiment is of interest the details are recorded in Table I.

The surface area of the crystals was estimated to be about 10,000 sq. cm. and, using the density data on liquid helium to make an estimate of the area occupied by a helium atom, it is found that about 1.3×10^{-5} mole would produce a monomolecular layer on the surface.

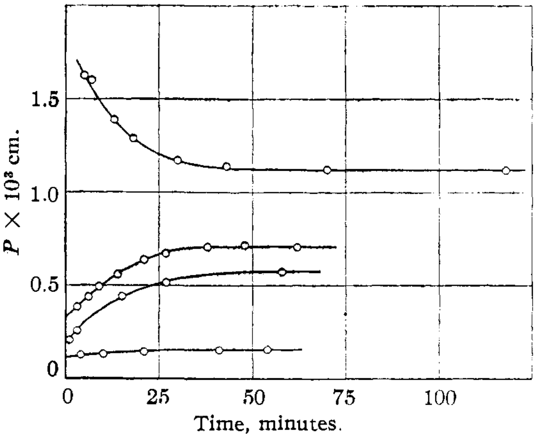

Fig. 1.—Adsorption pressure of helium gas on $NiSO_4 \cdot 7H_2O$ at 4.23°K.

The data at 4.23°K. are shown in Fig. 1, where it is evident that fairly complete equilibrium is obtained in about an hour.

It is of interest to estimate the heat of adsorption with the assistance of the Sackur–Tetrode equation. In making this calculation we will make use of the fact that liquid helium has a

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[1] (a) Giauque and MacDougall, THIS JOURNAL, **57**, 1175 (1935); (b) MacDougall and Giauque, *ibid.*, **58**, 1032 (1936).