The mother liquors from fraction B were concentrated to 60 cc. and 0.25 g. of salt (fraction E) obtained; m. p. 106–112°, $[\alpha]^{29}\text{D}$ 57.5 ± 0.5° (*c* 1.895, methanol).

The mother liquors from fraction E were concentrated to 30 cc. and 0.20 g. of salt (fraction F) obtained; m. p. 106–112°; $[\alpha]^{29}\text{D}$ 57.9 ± 0.5° (*c* 1.425, methanol).

Anal. Calcd. for $C_{20}H_{36}O_5N_3SBr$: C, 47.05; H, 7.11; N, 8.23. Found: C, 46.78; H, 7.19; N, 8.24.

The mother liquors from fraction F were evaporated to dryness and the residue taken up in dilute ethanol. The free 1-cyclononylsemicarbazide thus obtained showed no rotation in a methanol solution.

While the various fractions of salt showed slight differences in specific rotation, no evidence of activity in the free base was detected. This indicated that the variations in rotation of the various portions of the salt might well be due to differences in the concentrations used in determining their rotations. Fractions C and D seemed most likely to be pure and yet their specific rotations differed by 1.9°. If it is assumed that this difference is due to a dilution effect and all rotations are recalculated using a factor to offset dilution, the following values for $[\alpha]^{29}\text{D}$ (*c* 2, methanol) are obtained:

Fraction A, 57.1 ± 0.5°; Fraction C, 56.7 ± 0.5°; Fraction D, 56.7 ± 0.5°; Fraction E, 57.3 ± 0.5°; Fraction F, 56.9 ± 0.5°.

Summary

1. 1-Cyclooöctylsemicarbazide and 1-cyclononylsemicarbazide have been described.

2. The *d*-camphor-10-sulfonate and the *d*-α-bromocamphor-π-sulfonate of 1-cyclononylsemicarbazide were fractionally crystallized but no evidence of resolution was obtained.

URBANA, ILLINOIS RECEIVED MARCH 7, 1938

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

Amorphous Carbon Resistance Thermometer-Heaters for Magnetic and Calorimetric Investigations at Temperatures below 1°K.

BY W. F. GIAUQUE, J. W. STOUT AND C. W. CLARK

In various magnetic and calorimetric experiments in the region below 1°K. previously reported from this Laboratory magnetic susceptibility has been used to measure temperature. At the same time Giauque and MacDougall[1] pointed out that magnetic susceptibility is not appreciably useful for the purpose of denoting temperatures in the presence of any considerable magnetic field. Since in practice it is necessary to perform experiments at temperatures below 1°A. in a thermally isolated system, the only type of susceptibility which can be measured conveniently is the adiabatic susceptibility. The adiabatic differential susceptibility, $(\partial \mathbf{I}/\partial \mathbf{H})_S$, is of considerable importance in the application of thermodynamics to magnetic phenomena. **I, H** and *S* refer to the intensity of magnetization, field strength and entropy, respectively.

We recall[1a] that in an ideal paramagnetic system, at a temperature where the heat capacity due to the vibrations of the solid has approached zero, $(\partial \mathbf{I}/\partial \mathbf{H})_S$ is zero under all conditions. The reason for this is that the intensity of magnetization and entropy both depend on the magneton distribution among the various quantum states; thus constant *S* is equivalent to constant **I**. It is of interest to note that only the existence of magnetic interactions leading to nonideal paramagnetism, and a resultant heat capacity, has made it possible for the various experimenters to use magnetic susceptibility as a measure of temperature below 1°A.

At high fields the interionic magnetic interactions become nearly negligible in comparison with the applied field and the value of $(\partial \mathbf{I}/\partial \mathbf{H})_S$ does approach zero. This is shown experimentally by the curves in Fig. 1. The data used in plotting these curves have been taken from the work of Giauque and MacDougall.[2] The values of the adiabatic differential susceptibility are given as a function of magnetic field strength along constant entropy paths. Not only does Fig. 1 show that the quantity $(\partial \mathbf{I}/\partial \mathbf{H})_S$ drops to values too low to be of use in denoting temperature but it also shows that a given value of $(\partial \mathbf{I}/\partial \mathbf{H})_S$ does not uniquely determine a given value of temperature. Giauque and MacDougall[2] have also shown that data such as are illustrated in Fig. 1 may be used in combination with well-known thermodynamic equations to calculate the change of thermodynamic temperature along such an adiabatic path and thus one may know the temperature corresponding to any value of mag-

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[1] (a) Giauque and MacDougall, THIS JOURNAL, **57**, 1175 (1935); (b) Giauque, *Ind. Eng. Chem.*, **28**, 743 (1936); (c) Proc. VIIth Inter. Congress Refrig., (1936).

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

netic field if a reference point such as the temperature for zero field is known for the particular constant entropy path.

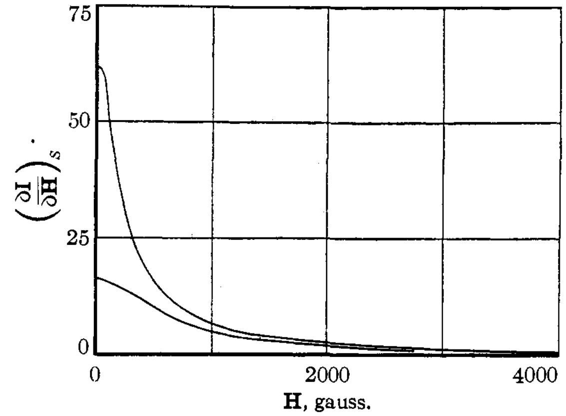

Fig. 1.—Adiabatic differential susceptibility of gadolinium phosphomolybdate tridecahydrate. $T_{(H=0)}$ is 0.126°K. for upper curve and 0.202°K. for lower curve.

This provides an excellent method of calibrating secondary thermometers but it is in many ways an unsatisfactory way of determining temperature during the course of an experiment involving a change of entropy due to heat leak or the introduction of energy for calorimetric purposes. In many cases it will be undesirable to disturb the experimental conditions by removing the field even for short intervals to find the particular entropy reference corresponding to each of a series of instantaneous observations in the experiment. To solve this problem we have sought a resistance thermometer which would be a suitable secondary standard.

The particular properties desired, in addition to a high temperature coefficient of resistance, are a very high specific resistance and a small change of resistance with magnetic field. The high specific resistance is desired because otherwise the alternating magnetic fields used for investigating magnetic properties would induce eddy currents and produce objectionable amounts of heat. Moreover, the use of a material of high specific resistance facilitates the construction of a thermometer of sufficiently high resistance so that extremely small electrical leads will not introduce appreciable error. Leads as small as possible are desirable to reduce thermal conductivity to a minimum. Such a thermometer could be used to introduce calorimetric energy and in many cases would be preferable to the induction type heater which we have investigated recently.[3] Although the induction type has the considerable advantage of not needing electrical leads, it cannot be used as a thermometer.

After a survey of the available resistance data we decided to investigate amorphous carbon. As is well known, this material decreases in resistance with increasing temperature. For example Hansen[4] has shown that the resistance of amorphous carbon decreases by 88% between 25 and 3500°C. and Kamerlingh Onnes and Clay[5] have shown that this effect continues even at the temperatures of liquid hydrogen. They found that from 273 to 20°K. the resistance of a carbon lamp filament increased by 23%.

Some preliminary experiments extending to 85°K. were tried with carbon ink films on glass and also with films deposited on a cold surface by an acetylene flame. The carbon ink films were heated to some 400–500°C. to drive off other constituents of the ink. We were surprised to find that such films increased in resistance by nearly 200% between 293 and 85°K. More complete experiments were performed on the carbon ink covered surface of glazed paper such as is commonly used in connection with quantitative analysis, and we believe that the characteristics of this material are typical of very finely divided carbon. Some results are given in Table I.

TABLE I

RESISTANCE OF CARBON INK AT LOW TEMPERATURES

Sample 1		Sample 2	
T, °K.	$R/R_{293°K.}$	T, °K.	$R/R_{293°K.}$
293	1.00	293	1.00
85	2.79	4.22	730
20.4	13.8	2.0	5,620
13.95	23.4	1.63	13,700
12.0	30.4		

No change in resistance with a magnetic field of 8000 gauss was found at 4.22 or at 2.0°; however, all of the exploratory measurements given in Table I were made with a low accuracy portable wheatstone bridge and all that can be concluded is that any change in a magnetic field was considerably less than 1%.

After the results given in Table I were obtained it was decided that carbon ink resistances were almost too much of a good thing. The sample increased from 57 to 780,000 ohms between 290

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(3) Giauque and Stout, THIS JOURNAL, **60**, 388 (1938).

(4) Hansen, *Trans. Am. Electrochem. Soc.*, **16**, 329 (1909).

(5) Kamerlingh Onnes and Clay, *Comm. Phys. Lab. Univ. Leiden*, No. 107c (1908).

and 1.63°K. with every indication that it would acquire much higher resistances below 1°K.

It has been shown by Kamerlingh Onnes and Hof[6] that the conductivity of compressed finely divided graphite decreases with temperature in the manner characteristic of pure metals. This, and the observations presented or quoted above, indicate that it should be possible to prepare carbon in a wide variety of forms so that the variation of resistance with temperature would be intermediate between T and $> 1/T$. Ordinary lampblack was a rather obvious choice in the search for a substance that would not attain such a high specific resistance as that of very finely divided carbon near 1°K.

For calorimetric work of high precision it is necessary to construct a thermometer that will be accurately reproducible, at least during the course of a series of experiments. At first sight lampblack and other finely divided forms of carbon may seem to present some difficulty in this connection, especially when one recalls the well-known unreliability of carbon resistances. This unreliability is particularly true of the most convenient form, a deposit of carbon on paper such as has often been used for grid leaks. However, consideration of the probable causes of the erratic variation of such resistances led to the conclusion that these effects would not be present at very low temperatures. Variation in the amount of adsorbed water is a rather obvious source of resistance variation at ordinary temperatures but not at low temperatures. At ordinary temperatures, the rather high coefficient of expansion of the paper often used as a base would, under the influence of temperature fluctuations, produce erratic changes in resistance. At very low temperatures coefficients of expansion approach zero. It appeared worth while to try an experiment with lampblack supported by paper. The reliability and usefulness of thermometers prepared in this way is such that their preparation will be described in more detail.

Preparation of Carbon Thermometer-Heaters.—The most convenient place to locate the carbon thermometer-heater was on the outside surface of the glass sample tube used in this work. A typical sample tube is about 2.5 cm. in diameter and 12 cm. in length. To avoid temperature lag effects, which might occur if ordinary paper were to be attached to a material of much smaller coefficient of expansion such as glass, lens paper was selected. This paper is of a very loose open structure.

To provide electrical connections, two platinum strips were deposited at one end of the sample tube and thin glass platinized leads about 14 cm. long and 0.13 cm. in diameter in the form of rounded N's were used to connect the thermometer to tungsten terminals sealed through the outer glass wall which enclosed the insulating vacuum space. A piece of fine platinum wire was used to connect the tungsten terminals to the glass N's.

A single layer of lens paper, 0.004 cm. in thickness, was applied to the sides of the glass sample tube by means of ethyl alcohol and a camel hair brush. While the paper was still wet, lampblack mixed with a large amount of alcohol was painted into the paper. A coating of collodion was applied in the form of a dilute solution in alcohol and ethyl ether. Excess paper was then cut from the tube until the thermometer remained in the form of an inverted U extending from top to bottom on the tube. The resistance was adjusted by reducing the width of the conducting strips until the desired order of magnitude was obtained. The final strips were about 1.5 cm. wide. In the adjustment of the resistance allowance had to be made for the effect of drying the collodion. For example, a thermometer-heater which had just been prepared decreased in resistance from 200,000 ohms to about 50,000 ohms on standing overnight. Thereafter the resistance proved to be surprisingly stable. A layer of lens paper was then applied to the whole side surface of the sample tube and attached with the dilute collodion solution. This served very well to hold the conducting strips in place.

The shape of the heater was selected so that magnetic induction would be at a minimum and the thin platinized glass connecting leads were scraped on two sides for the same reason. The resistance of similar platinized leads was measured down to 13.9°K. and the measurements show that they represented but a small fraction of the total resistance. Thus the uncertainty due to energy developed in the leads during electrical heating was negligible. The data on a typical platinized lead are given in Table II.

TABLE II

RESISTANCE OF PLATINIZED GLASS HEATER-THERMOMETER LEAD

T, °K.	298	85	20.3	13.9
R, ohms	63.1	40.0	33.6	33.6

Characteristics of Carbon Thermometer-Heaters.—Four similar carbon thermometer-heaters have been studied. However, only one thermometer, No. 4, was investigated below 1°K. The measurements on the others extended only to about 1.5°K. In Table III a series of observations on thermometer-heater No. 4 is presented. The data may be taken as typical. A thermometer current of about 4×10^{-7} ampere was used for the measurements.

The data are shown in Fig. 2.

The observations given in Table III were obtained with a sample tube filled with gadolinium phosphomolybdate tridecahydrate. The previous work of Giauque and MacDougall[2] on this sub-

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[6] Kamerlingh Onnes and Hof, *Comm. Phys. Lab. Univ. Leiden*, No. 142b (1914).

TABLE III

THE RESISTANCE OF A CARBON THERMOMETER AS A FUNCTION OF TEMPERATURE

T, °K.	R, ohms	T, °K.	R, ohms
0.129	58640	1.659	41303
.245	52584	1.836	40843
.316	51083	2.365	39829
.482	48715	4.227	37767
.608	47345	13.92	34851
.750	46122	17.83	34357
.919	44780	20.24	34129
1.144	43338	60.6	32015
1.397	42196	293 ± 5	28062

stance made it possible to obtain temperatures below 1°K. from measurements of the magnetic susceptibility. Temperatures above 1°K. were obtained from the vapor pressures of helium, hydrogen and oxygen.

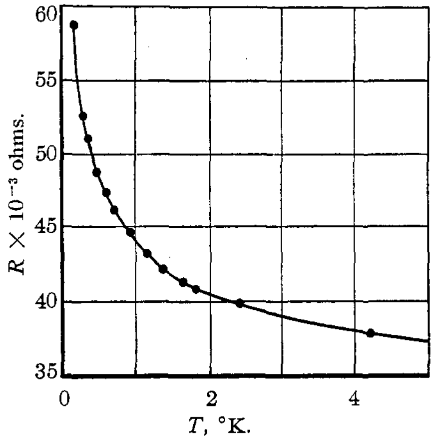

Fig. 2.—The resistance of a carbon thermometer as a function of temperature.

When the sample was demagnetized the carbon thermometer decreased in temperature to 0.129°K. with great rapidity, and it appeared to be in rather good equilibrium with the sample temperature. However, the thermometer then started to warm more rapidly than the sample. This was determined by a simultaneous series of magnetic susceptibility and resistance measurements. It appears that a small portion of the moist gadolinium phosphomolybdate crystals adhered to the outer wall of the sample tube and was thus in good thermal contact with it, although the main body of the sample was separated from the wall by a very appreciable thermal resistance. Since the sample tube and carbon thermometer-heater had no appreciable heat capacity, they were easily cooled to the lowest temperature produced by the adiabatic demagnetization of the sample but soon warmed by as much as several hundredths of a degree in advance of the main body of the gadolinium phosphomolybdate. This was because the small amount of material attached to the glass wall absorbed more than its share of the heat leak. The above effect occurred at temperatures below 0.2°K. and may have caused some small error up to 0.3°K. At higher temperatures the helium gas pressure in the tube appeared to have become sufficient to permit equilibrium. There should not be much error in the observation at 0.129°K. in Table III and any error would be such as to have given too low a value of the resistance.

Accurate measurements of any kind at these temperatures will necessitate some artifice for securing equilibrium distribution throughout the sample. It may be noted that this is not a problem that can be solved by placing the thermometer-heater within the sample tube or by introducing energy uniformly throughout the sample as can be done by means of radioactive energy. Accurate measurements will also require the uniform distribution of heat leaking in from the surroundings. Although the heat leak can be made extraordinarily small it is still very appreciable in comparison with the total amounts of energy concerned in calorimetric measurements at these temperatures. The problem is not one relating particularly to any form of thermometer and we will not discuss it here except to state that the present observations indicate that the thermometer comes rapidly to equilibrium with the glass surface to which it is attached.

In constructing Thermometer No. 4 on the gadolinium phosphomolybdate sample tube it was not possible to use the platinizing technique employed on the other thermometers as it involved heating the surface. It was desired to use the sample of gadolinium phosphomolybdate which had been investigated by Giauque and MacDougall[2] and this compound is rather easily decomposed when heated. To avoid this the electrical contact with the carbon was established by means of strips of silver deposited by a silvering solution. The thickness of a similar silver surface was determined to be 2×10^{-5} cm. Although the amount of heat developed in the silver by the alternating magnetic fields used for magnetic susceptibility measurements was very small, it proved to be a considerable handicap. The usual measurements with the inductance bridge involved the application of a 60 cycle root mean square magnetic field of 20 gauss for about 10 sec. Under these circumstances it was estimated that the silver developed about 10^{-8} cal./sec. in such close proximity to the heater that it produced a temporary disturbance in the thermometer, which had a very small heat capacity. The amount of heat was estimated by subjecting the sample tube to a 60-cycle, root mean square, field of 360 gauss. In this case the heat could be observed calorimetrically.

No effect of the kind mentioned above was noted with the other thermometers nor would any be expected when the known resistance of the platinized glass is taken into consideration.

It is of interest to consider the amount of heat which may have been developed within the carbon thermometer itself when an alternating magnetic field was applied. The specific resistance was probably largely due to the small contact areas and it was of course too high to permit the development of appreciable heat by the flow of eddy currents throughout the powder.

The particles of lampblack were too small to be observed by an ordinary microscope and the particle size may be estimated at 10^{-4} cm. or less. However, the specific resistance within the particles was undoubtedly very much lower than that throughout the powder and if they were at all graphitic in nature the specific resistance, ρ, may have dropped to a rather low value. From the work of Kamerlingh Onnes and Hof[6] on the resistance of compressed graphite at various temperatures down to 14°K., the measurements of de Haas and van Alpen[7] from 20 to 1°K. and the specific resistance of single crystal graphite as determined by Ryschkewitsch,[8] one may estimate very roughly that $\rho = 10^{-5}$ ohm cm. near 1°K.

The magnitude of the heat developed by the alternating magnetic fields used for inductance measurements may be obtained from the following considerations. Let $\mathbf{H}_1$ be the applied field at time t and $\mathbf{H}_2$ be the instantaneous field due to eddy currents in the particles. Then

$$\mathbf{H} = \mathbf{H}_1 - \mathbf{H}_2 \tag{1}$$

where $\mathbf{H}$ may be taken as the net field acting on any given particle. In the present problem sufficient accuracy can be obtained with the usual approximation[9]

$$\mathbf{H}_2 = 4\pi/3\ \Sigma\ \mathbf{M} \tag{2}$$

where in the present case $\Sigma\ \mathbf{M}$ refers to the summation of the magnetic moments due to eddy currents in all the particles in 1 cc.

It may be shown that the self inductance of the individual particles may be neglected in comparison with the summed effect of all the particles; thus, the current distribution within a single particle may be found from resistance considerations alone.

For simplicity we may assume that the particles are spheres and all of the same size.

Then it may be shown that the magnetic moment of a sphere

$$\mathbf{M} = \frac{2\pi r^5}{15\rho}\frac{\mathrm{d}\mathbf{H}}{\mathrm{d}t} \tag{3}$$

where r is the radius of the sphere and ρ the specific resistance.

$$\mathbf{H}_1 = \mathbf{H}_0 \sin \omega t \text{ where } \omega = 2\pi f$$

f = frequency in cycles/sec. From equations 1, 2 and 3

$$\mathbf{H} = \mathbf{H}_0 \sin \omega t - \frac{8\pi^2 n r^5}{45\rho}\frac{\mathrm{d}\mathbf{H}}{\mathrm{d}t} \tag{4}$$

where n is the number of particles in 1 cc.

From equation 4

$$\mathbf{H} = \mathbf{H}_0 \cos\phi \cdot \sin(\omega t - \phi) \tag{5}$$

and

$$\frac{\mathrm{d}\mathbf{H}}{\mathrm{d}t} = \mathbf{H}_0\omega \cos\phi \cdot \cos(\omega t - \phi) \tag{6}$$

where

$$\tan\phi = \frac{8\pi^2 n r^5 \omega}{45\rho} \tag{7}$$

The heat developed in n spheres[3] in unit time is given by

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{2\pi n r^5}{15\rho}\left(\frac{\mathrm{d}\mathbf{H}}{\mathrm{d}t}\right)^2 \text{ erg./sec.} \tag{8}$$

$\mathrm{d}\mathbf{H}/\mathrm{d}t$ may be replaced by

$$\omega\overline{\mathbf{H}} = \omega\overline{\mathbf{H}}_0 \cos\phi \tag{9}$$

where $\overline{\mathbf{H}}$ and $\overline{\mathbf{H}}_0$ refer to the root mean square averages of the magnetic fields. Combining equations 7, 8 and 9

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{3\omega}{8\pi}\overline{\mathbf{H}}_0^2 \sin 2\phi \tag{10}$$

$$= \frac{3}{4} f\, \overline{\mathbf{H}}_0^2 \sin 2\phi \text{ erg./sec. cm.}^3 \tag{11}$$

In the above equations all quantities are to be expressed in e. m. u. The number of particles in the thermometer is estimated approximately as 10^{11} corresponding to a thermometer volume of 0.1 cc. Assuming the particles to have the conductivity of graphite and using the approximate value, $\rho = 10^{-5}$ ohm cm., given above, and $\overline{\mathbf{H}}_0 = 20$ gauss

$$\mathrm{d}q/\mathrm{d}t = 2 \times 10^{-15} \text{ cal./sec.}$$

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(7) De Haas and van Alpen, *Comm. Phys. Lab. Univ. Leiden*, Comm. 212e (1938).

(8) Ryschkewitsch, *Z. Elektrochem.*, **29**, **474** (1923).

(9) See, *e. g.*, Starling, "Electricity and Magnetism," Longmans, Green and Co., London, 1921, p. 269.

In fact even if the conductivity within the particles is taken equal to the greatest conductivity observed in pure non-superconducting metals at a few degrees absolute, $\rho = 10^{-9}$ ohm cm. dq/dt becomes only 2×10^{-11} cal./sec. The experimental observations mentioned above show that this amount of energy would have produced no observable effect on the carbon thermometer.

The Reproducibility of the Carbon Thermometer.—It is evident that a carbon thermometer of the type described here could not be expected to retain its calibration after it has been warmed to ordinary temperatures and again cooled to liquid helium temperatures at a later date. However, after some aging the carbon thermometers proved to be much more reproducible than had been expected and, of more importance, no significant change of resistance with time occurred when the thermometer was kept cold continuously for thirty hours.

To show the order of magnitude of the change with time some data on Thermometer No. 4 are presented in Table IV. The values at room temperature were taken merely to ensure that the circuits were working properly before the start of an experiment; thus they may have been affected by several tenths of a per cent. by variation of the room temperature which was not measured. The dR/dT at 293 was about 7 ohms per degree. The ratio of the resistance at 4.200°K. to the room temperature resistance is given in column 4 of Table IV. The ratio is remarkably constant and we believe that most of the small changes are due to the variation of room temperature. Some of the variations of the resistance itself are undoubtedly due to mechanical effects from handling the apparatus.

TABLE IV

VARIATION OF THE RESISTANCE OF A CARBON THERMOMETER WITH TIME

Date 1936	R, ohms Room T	R, ohms at T	T, °K.	$R_{4.200°\text{K.}}/R_{\text{Room } T}$
Feb. 14	26,858	36,196	4.234	1.349
May 16	—	38,142	4.221	—
22	28,187	38,072	4.218	1.351
June 12	28,090	37,878	4.218	1.349
20	28,134	37,931	4.224	1.349
Nov. 27	27,924	37,636	4.2	1.348
Dec. 5	28,106	37,817	4.234	1.346
19	28,062	37,767	4.227	1.347

Values of the resistance over a period of time, during one cooling for Thermometer No. 3 at the boiling point of helium, are given in Table V.

TABLE V

REPRODUCIBILITY OF A CARBON THERMOMETER KEPT AT LOW TEMPERATURES

Time, hrs.	R at b. p. of He, ohms.
0.0	77,106
.45	77,114
.78	77,104
1.03	77,105
21.72	77,117
29.60	77,113
	Av. 77,110 ± 0.006%

Between the times 1.03, 21.72 and 29.60 the thermometer was at various temperatures between 1.5 and 20°K. The resistance at the boiling point of helium always returned to the same value to within 0.006%.

Another type of test of reproducibility was made by passing a much larger current through the thermometer-heater than would be used for an ordinary calorimetric energy input. No hysteresis in the resistance could be detected. The test was made on Thermometer-Heater No. 2 at the boiling point of helium with a small amount of helium gas in the insulating vacuum space about the calorimeter. The data are listed in Table VI.

TABLE VI

TEST SHOWING THE ABSENCE OF RESISTANCE HYSTERESIS DUE TO THE PASSAGE OF AN ELECTRICAL CURRENT IN A CARBON THERMOMETER-HEATER

Time, min.	R, ohms $T = 4.22$°K.
0	58,736
58	58,744
63-73	$I = 4.5 \times 10^{-4}$ amp.
75	58,738
82	58,741

The observations show that the resistance, after the passage of 4.5×10^{-4} amperes for ten minutes, was unchanged within 0.005%.

While the energy measuring system was not intended for accurate resistance determinations the energy measurements did allow the calculation of the resistance while the 4.5×10^{-4} ampere heating current was flowing. The value found, 58,710 ohms, is within the limit of accuracy with which the two measuring systems were known. It may be stated that Ohm's law was obeyed to within 0.05%. A current of about 2.2×10^{-5} ampere was used for the resistance measurements given in Table VI.

The Effect of a Magnetic Field on the Resistance of Carbon Thermometers.—As mentioned above, one of the principal reasons for investigating the carbon thermometer was the development of a means of measuring temperature in the presence of magnetic fields. For this reason it is of importance to study the effect of a magnetic field on the resistance. The effect was studied with Thermometers Nos. 1, 2 and 3, and in each case the magnitude was about the same. Except for a small portion of the circuit, the current and field were parallel. The data are presented in Table VII. It had been hoped to extend the observations on the change of resistance with a magnetic field to the region below 1°K. by means of Thermometer No. 4, which was on the gadolinium phosphomolybdate sample tube. The effect must be studied in combination with the large effect due to temperature increase when a field is applied at temperatures below 1°K., and the few observations which were made under poor conditions are not sufficiently complete to determine the effect accurately. However, it may be stated that the effect does not become very large down to 0.4°K. The effect of a magnetic field on resistance at temperatures below 1°K. will be investigated later.

TABLE VII

THE CHANGE OF RESISTANCE OF CARBON THERMOMETERS IN A MAGNETIC FIELD

H gauss	T, °K.	$\Delta R \times 10^4/R$	Calcd. $\Delta R \alpha \mathbf{H}^2$	Remarks
		Thermometer No. 1		
8200	1.5	26.2	(26.2)	
4000	1.5	6.4	6.2	
		Thermometer No. 2		
8300	4.23	4.2	(4.2)	
5960	4.23	2.2	2.2	
4000	4.23	1.0	1.0	
		Thermometer No. 3		
8360	4.23	5.27	(5.27)	6–5–35
6610	4.23	3.37	3.30	$R_{290} = 62{,}000$
4930	4.23	1.84	1.83	
3330	4.23	0.83	0.82	
1630	4.23	.19	.20	
8200	1.5	28.4	(28.4)	6–19–35
6240	1.5	16.3	16.4	$R_{290} = 57{,}908$
8260	4.22	4.68	(4.68)	1–8–36
6200	4.22	2.61	2.64	$R_{290} = 57{,}537$
3270	4.22	0.73	0.73	

The data in Table VII show that the increase in resistance is proportional to the square of the applied field between 1.5 and 4.22°K. and the effect is increasing with decreasing temperature. The dependence of ΔR on $\mathbf{H}^2$ should greatly simplify the necessary thermometric corrections.

We thank Dr. C. J. Egan for assistance with some of the measurements.

Summary

The problem of secondary standards for the measurement of temperature below 1°A. in the presence of a magnetic field has been discussed. The electrical resistance characteristics of finely divided amorphous carbon at low temperatures has been investigated and it has been concluded that amorphous carbon resistance thermometer-heaters will be very useful at temperatures below 1°K.

At 1.63°K. a carbon ink thermometer had an electrical resistance 13,700 times as great as the resistance at 293°K. The rate of increase with decreasing temperature was accelerating so rapidly at 1.63° that it appeared desirable to use a form of carbon with a smaller temperature coefficient of resistance.

The construction of amorphous carbon thermometer-heaters from lampblack is described.

The problem of possible heat development by eddy currents within the carbon particles during measurements requiring the presence of alternating fields has been discussed. Even if the conductivity of the lampblack particles is assumed to be as great as that of graphite at low temperatures, a measuring field of 20 r. m. s. gauss would produce only the negligible quantity of heat 2×10^{-15} cal./sec.

The resistance of platinum films on glass has been investigated at low temperatures in connection with their use as thermometer-heater leads.

The resistance of a carbon thermometer has been determined from 293 to 0.129°K. The resistances at these temperatures were 28,062 and 58,640 ohms, respectively.

The resistance of one thermometer which was studied over a period of a year was constant to a per cent. after the initial stabilization had taken place. The ratio of the resistance at the boiling point of helium to that at room temperature was constant to a few tenths of a per cent. during the year and it seems probable that this variation was due to the unmeasured variations of room temperature. It was, of course, not expected that the thermometer would retain its calibration during successive coolings from room temperature. A test of reproducibility during a thirty-hour series of measurements at liquid helium temperatures showed a variation of only 0.006%.

No resistance hysteresis was found following the passage of a current.

The increase of resistance in a magnetic field was measured at 4.2 and 1.5°K. It was found to be larger at the lower temperature and proportional to the square of the applied field at both temperatures.

BERKELEY, CALIF. RECEIVED FEBRUARY 14, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

The Fluorination of Aliphatic Substances with Mercurous Fluoride

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Mercurous fluoride, correctly prepared and used,[1-6] is a valuable fluorinating agent but excessive claims and implications have been made for it and it is therefore the purpose of this paper to describe in detail a convenient laboratory preparation of the pure, anhydrous salt, to outline the limitations of its use, and to present a simple method which circumvents some of its defects.

Preparation of Mercurous Fluoride.—Previously described methods of preparation are unreliable, time-consuming and yield products whose analyses (when reported) demonstrate the presence of water and oxides. The use of organic solvents in washing and drying does not make any improvement, and chemical reagents less than "chemically pure" cause unneeded complications.

First mercurous nitrate is prepared by dissolving 40 g. of red mercuric oxide in a mixture of 28 cc. of concentrated nitric acid and 60 cc. of water. This solution is shaken vigorously in a bottle with 40 g. of mercury, until the mercury ceases to dissolve readily, at which point mercurous nitrate starts to crystallize out. A solution of 4 cc. of concentrated nitric acid in 45 cc. of water is then added to redissolve the crystals, and the excess of mercury is decanted. The solution is next poured into a freshly prepared solution of 48 g. of potassium bicarbonate in 200 cc. of water, and the resulting mercurous carbonate is filtered by suction in the presence of a few pieces of solid carbon dioxide, and finally washed thoroughly with 1400 cc. of water saturated with carbon dioxide. All operations should be carried out in diffused light. The moist mercurous carbonate is added immediately, in small portions and with constant stirring, to a mixture of 100 cc. of 48% hydrofluoric acid and 260 cc. of water, in a platinum dish, which is then heated on the water-bath, with gentle stirring, until a dry, sandy powder is obtained. This powder, which is quite friable, is rapidly scraped off the walls, coarsely crushed under the bottom of a platinum crucible, and then heated for an hour on the water-bath. The salt should be removed from the dish and stored immediately in tightly stoppered copper or resin containers. The yield is about 80 g. Analysis indicates 91.28% mercury and 8.86% fluorine. Theory requires 91.35% mercury and 8.65% of fluorine.

Fluorination Procedure.—In addition to the described procedures[1-6] it is possible to operate substantially as described for mercuric fluoride,[7] particularly when the compound to be fluorinated boils at a temperature lower than the threshold at which fluorination proceeds. Fluorination with mercurous fluoride is lively, but never as violent as with mercuric fluoride.

Limitations.—Mercurous fluoride gives generally very good yields of alkyl monofluorides from alkyl monoiodides and good yields from bromides; from polyiodides, it gives very poor yields of polyfluorides; from polybromides, the results were as follows: ethylidene bromide yielded vinyl bromide, and so also did ethylene bromide; 1,1,2-tribromoethane yielded a mixture of $CHFBrCH_2Br$, $CH_2{=}CBr_2$ and $CHBr{=}CHBr$, with the latter two substances far predominant; acetylene tetrabromide gave a very small quantity of $CHBrFCHBr_2$, contaminated by ethylenic and acetylenic decomposition products and their polymers. In general the reaction with polybromides starts between 120 and 140°. Polychlorides, when affected at all, lose hydrochloric acid.

From Mercurous to Mercuric Salt.—A method to circumvent some of the fluorination difficulties is to cause a transformation of the mercurous fluoride into a mercuric salt. The high fluorinating power of mercuric fluoride, even at low temperature, has been described before.[8] This transformation was performed very simply by Swarts,[4] while preparing methyl fluoride, by dissolving one gram atom of iodine in a large amount of methyl iodide and progressively feeding one gram molecule of mercurous fluoride into the solution, presumably causing the formation of one gram molecule of mercuric fluoroiodide; the latter produced a gram molecule of methyl fluoride with an 80% yield.

This method has now been extended to polybromides and polyiodides, and the qualitative results obtained were those which would have prevailed had mercuric fluoride been used; the difference appears only in yields and ease of operation, and consequently the use of an equimolecular mixture of mercurous fluoride and iodine can be regarded as a substitute for the use of mercuric fluoride. Ethyli-

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[1] Swarts, *Bull. acad. roy. Belg.*, [3] **31**, 675–688 (1896).

[2] Swarts, *Bull. soc. chim. Belg.*, **30**, 302 (1921).

[3] Desreux, *ibid.*, **44**, 1 (1935).

[4] Swarts, *ibid.*, **46**, 10–12 (1937).

[5] Ruff and others, *Ber.*, **69B**, 299 (1936).

[6] Van Arkel and Zanetzky, *Rec. trav. chim.*, **56**, 167 (1937).

[7] Henne, THIS JOURNAL, **59**, 1200 (1937).

[8] Henne and Midgley, *ibid.*, **58**, 884 (1936).