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

The Effect of a Magnetic Field upon the Electrical Resistance of Gold and Silver at Temperatures between 1 and 20°K.

BY J. W. STOUT AND R. E. BARIEAU

It has been found recently by Giauque, Stout and Clark[1] that gold wire containing a small amount of silver exhibited at 1.63°K. a decrease in electrical resistance when a magnetic field was applied. The only metals previously known to have a negative magnetic coefficient of resistance were ferromagnetic, and the decrease in resistance in those cases was believed related in origin to phenomena such as magnetostriction. Present theories of electrical conductivity[2] predict that a magnetic field will always cause an increase in resistance. The experiments of Giauque, Stout and Clark[1] were primarily designed to investigate materials suitable for induction heaters at low temperatures. The anomalous behavior of the nearly pure gold wire was discovered incidentally and measurements of the magnetic change in resistance were made only at two temperatures. In view of the abnormal behavior of gold it was decided to investigate in more detail the effect of a magnetic field upon the resistance of another sample. Measurements were also made upon a sample of silver.

Preparation and Mounting of the Gold and Silver Wires.—The gold wire, No. 40 B. and S. gage, was obtained from a commercial manufacturer and was guaranteed to contain no more than 0.01% of impurities. The resistance of the wire at low temperatures led us to believe that the gold contained a greater amount of impurity than this. Accordingly after the completion of the measurements we sent the gold wire to the U. S. Mint for assay. The Mint reported that the sample contained 99.84% gold. In addition we analyzed a sample of the gold wire by means of colorimetric tests. These showed the presence of 0.12% Ag, 0.002% Cu and 0.006% Fe. The sample of gold wire used in the previous experiments[1] and which was thought to contain about 0.1% Ag was also analyzed colorimetrically. It contained 0.19% Ag, 0.001% Cu and 0.009% Fe. The silver wire was made from electrolytic silver which was 99.99% pure. It was drawn into wire by a commercial manufacturer. The wire after drawing contained 0.008% Cu and 0.004% Fe.

The wires were wound non-inductively on grooved bakelite cylinders. The direction of the magnetic field was parallel to the axis of the cylinders and therefore perpendicular to the direction of the current in the wires. Copper current and potential leads were soldered to each end of the wires.

The thermal expansion of the bakelite (Dilecto Grade XX) cylinder was measured between 80 and 300°K. Between these temperatures the average linear coefficient of expansion was 2.1×10^{-5} deg.$^{-1}$. The thermal expansions of gold and silver are slightly less than this value. The wire was loosely wound on the bakelite and since it would shrink less on cooling than the bakelite no strains could have been introduced due to the change in temperature.

The gold and silver wires, after being drawn, were annealed in vacuum on glass spools for three hours at 450°C. They were then wound on the bakelite cylinders, and annealed by passing through them a current sufficient to heat them to the necessary temperature. The temperature of the wire was estimated from its resistance. The gold was annealed for four hours at 120°C. and the silver for two hours at 150°C. During the annealing the coils were immersed in an atmosphere free from air and containing about 2 mm. pressure of helium. The wires were subjected to no mechanical stresses after the final annealing.

Apparatus.—The bakelite cylinders on which the wires were wound were mounted in the center of the iron-free solenoid type magnet described by Giauque and MacDougall.[3] The cylinders were surrounded by a dewar vessel into which liquefied helium or hydrogen could be introduced. The vapor pressure of the bath was controlled by a mercury manometer actuating a magnetic valve leading to a vacuum pump. The temperature of the wire was determined from the vapor pressure of the bath, using the equations of Keesom and co-workers[4] for helium, of Palacios Martinez and Kamerlingh Onnes[5] for liquid hydrogen and of Giauque, Johnston and Kelley[6] for solid hydrogen. The bath was not provided with a stirrer so in order to prevent errors due to temperature gradients in the liquid the bath was always heated by means of an electrical heater in the bottom of the dewar or cooled by evaporating liquid from the top. In either case convection currents are set up which will ensure temperature equilibrium. For liquid helium below the temperature of maximum density the phenomenally high heat conductivity discovered by Keesom and Keesom[7] would ensure temperature equilibrium.

The resistance was measured by comparing with a White potentiometer the potential drop across the sample of gold or silver with that across a standard resistance in series with the gold and silver coils. Thermoelectric effects were determined by measuring the potential drop across the coils when no current was flowing. The thermoelectric potentials were extremely small, in the largest case only

(1) (a) Giauque, Stout and Clark, *Phys. Rev.*, **51**, 1108 (1937); (b) Giauque and Stout, THIS JOURNAL, **60**, 388 (1938).

(2) See, *e. g.*, Wilson, "The Theory of Metals," Cambridge, 1936, p. 166.

(3) Giauque and MacDougall, THIS JOURNAL, **57**, 1175 (1935).

(4) (a) Keesom, Weber and Schmidt, *Comm. Phys. Lab. Univ. Leiden*, No. 202c; (b) Keesom, *ibid.*, No. 219a.

(5) Palacios Martinez and Kamerlingh Onnes, *Comm. Phys. Lab. Univ. Leiden*, No. 156b.

(6) Giauque, Johnston and Kelley, THIS JOURNAL, **49**, 2367 (1927).

(7) Keesom and Keesom, *Physica*, **3**, 359 (1936).

TABLE I

RESISTANCE AND CHANGE IN RESISTANCE WITH A MAGNETIC FIELD FOR GOLD AT LOW TEMPERATURES

T, °K.	$\frac{R_T}{R_{273.1°K.}}$ (H = 0)	$\Delta R \times 10^4/R_{273.1°K.}$ Magnetic field strength in gauss 900	1100	1600	2500	3200	6000	8000
1.548	0.066259	0.113	...	0.313	0.710	1.12	3.05	4.61
1.568	.066240	.105	...	.314	.749	1.16	3.14	4.76
1.920	.065949	.148	...	.420	.978	1.52	4.27	6.55
2.671	.065521	.176	...	.525	1.225	1.91	5.45	8.51
3.485	.065193	.204	...	.595	1.347	2.12	6.07	9.53
4.214	.064990	.201	...	.655	1.428	2.24	6.40	10.11
10.66	.064901	...	0.281	.562	1.320	2.17	6.44	10.42
13.92	.066242	...	0.244	.536	1.222	1.99	5.96	9.66
20.34	.073062	.106	...	.372	0.860	1.38	4.56	7.51

TABLE II

RESISTANCE AND CHANGE IN RESISTANCE WITH A MAGNETIC FIELD FOR SILVER AT LOW TEMPERATURES

T, °K.	$\frac{R_T}{R_{273.1°K.}}$ (H = 0)	$\Delta R \times 10^4/R_{273.1°K.}$ Magnetic field strength in gauss 900	1100	1600	2500	3200	6000	8000
1.543	0.019420	0.215	...	0.610	1.40	2.22	6.66	10.67
1.558	.019420	.214	...	.616	1.40	2.23	6.63	10.66
1.920	.019420	.220	...	.618	1.42	2.24	6.66	10.64
2.671	.019421	.219	...	.617	1.42	2.22	6.68	10.63
3.485	.019423	...	0.309	.614	1.40	2.22	6.63	10.59
4.214	.019426	.213	...	.616	1.39	2.23	6.63	10.57
10.67	.019708	...	.293	.590	1.34	2.15	6.48	10.26
13.92	.020254	...	.280	.554	1.28	2.09	6.18	10.03
20.34	.023219	...	.246	.496	1.12	1.81	5.68	8.94

amounting to 0.014% of the total measured potential. The absolute accuracy with which the resistance could be measured was about 0.01%. However, the precision of the potentiometer was much greater than this so that small changes in resistance could be measured to an accuracy of about 0.001% of the total resistance. A measuring current of 6×10^{-3} ampere was used.

The magnetic field was calculated from the current passing through the magnet coils and their geometry. The current was read on a calibrated ammeter to an accuracy of about 0.5%.

The ice-point resistances were measured after the completion of the other experiments. The coils were removed from the magnet dewar and placed in kerosene which was cooled with an ice-bath. The temperature of the kerosene was measured with a calibrated mercury thermometer and found to be 0 °C. within the accuracy of the thermometer (about 0.01°). The ice-point resistance of the gold wire was 113.801 ohms and of the silver 98.841 ohms.

The Results.—The data for the gold wire are presented in Table I and those for the silver in Table II. For each temperature the resistance in zero field is given together with the change in resistance for various field strengths. The resistance at the ice point is taken as the unit in each case. The observations in the magnetic fields were taken at field strengths differing slightly from those in the tables. For each temperature a plot was made of $\Delta R/\mathbf{H}^2$ vs. **H** and the smooth curve through the points was used to calculate the correction necessary to convert each observed ΔR to that corresponding to one of the even fields listed in the table. In all cases the correction was known with an accuracy exceeding that of the measured ΔR's.

Figure 1 shows the resistance in various field strengths as a function of temperature for gold.

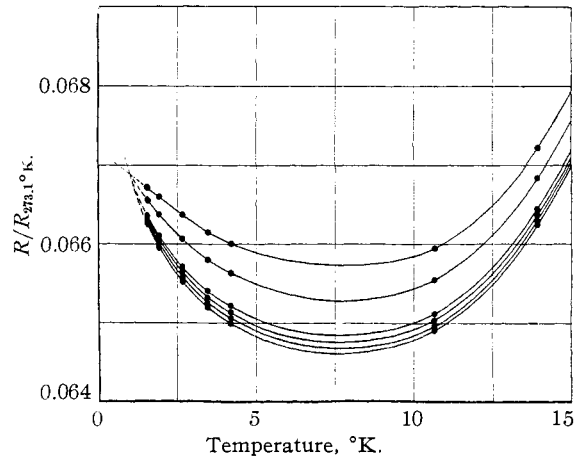

Fig. 1.—Resistance of gold in various magnetic fields. The curves, reading from the bottom, are for fields of 0, 1600, 2500, 3200, 6000 and 8000 gauss, respectively.

Figure 2 presents the corresponding data for silver. In order to show more clearly the behavior at low temperatures the curves have been extended only to 15°K. At the lowest temperatures both the

resistance of the silver and its magnetic coefficient are independent of the temperature. As the temperature rises the temperature coefficient of resistance is positive and rapidly increasing while the magnetic coefficient decreases slightly although always remaining positive. The magnetic change in resistance is intermediate between a linear and quadratic function of the field although it approaches more closely the latter.

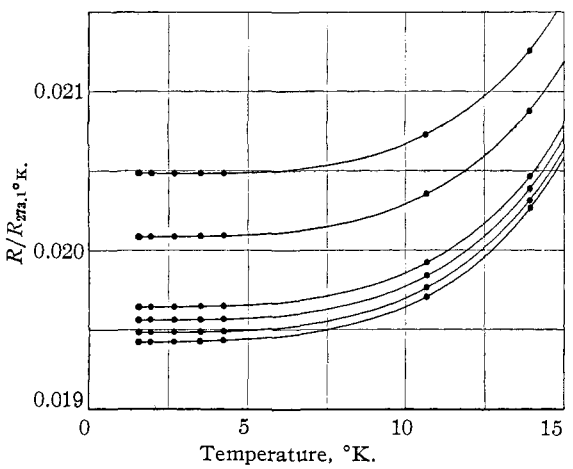

Fig. 2.—Resistance of silver in various magnetic fields. The curves, reading from the bottom, are for fields of 0, 1600, 2500, 3200, 6000 and 8000 gauss, respectively.

The resistance–temperature curve of the gold shows the minimum in resistance previously found by de Haas and co-workers[8] and by workers[1] in this Laboratory. De Haas and co-workers have found that the ratio $R_{\text{min.}}/R_{273.1°\text{K.}}$ is a smooth function of the temperature of the minimum, the minimum shifting to lower temperatures as the residual resistance decreases. Their samples of gold all had a lower residual resistance than that investigated in this research, probably because of a larger amount of impurity in our sample. Since the primary object of this experiment was to investigate the anomalous behavior of gold below the minimum it is fortunate that the gold contained more impurity than we had expected. For purer gold the whole phenomenon would have been shifted to a lower temperature and could not have been as completely investigated at the temperatures readily obtainable with liquid helium. The ratio $R_{\text{min.}}/R_{273.1°\text{K.}}$ when plotted against T min. falls on a reasonable extension of their curve both for the sample used in this research and for that previously investigated.[1] In the present case the temperature of the minimum is about 7.7°K. and the ratio $R_{\text{min.}}/R_{273.1}$ is 0.0646.

In a magnetic field the dip in resistance becomes less pronounced. The resistances for different magnetic fields appear to converge to a common value at about 1°K. At this temperature the magnetic field would have no effect upon the resistance while at lower temperatures it would presumably cause a decrease in resistance. Such a decrease in resistance was found at 1.63°K. for the sample of gold previously investigated[1] in this Laboratory, while at 4.23°K. the magnetic coefficient was positive.

The change in resistance of the gold varies as the square of the field for the highest temperatures and lowest fields investigated. At larger fields and at the lower temperatures the variation in resistance is intermediate between the first and second powers of the field.

The effect of a magnetic field upon the resistance of a gold wire and upon single crystals of gold has also been investigated by Meissner and Scheffers.[9] They report no evidence of a minimum in resistance although from the residual resistance of their wire we should expect one to occur at about 7°K.

It has been suggested by Kapitza[10] that the magnetic change of resistance should obey a law

$$\frac{\Delta R}{R_{273}} = \beta \frac{\mathbf{H}^2}{3\mathbf{H}_k}$$

when $\mathbf{H}$ is small compared to $\mathbf{H}_k$. When $\mathbf{H}$ is large compared to $\mathbf{H}_k$ the change of resistance should be given by the expression

$$\frac{\Delta R}{R_{273}} = \beta\left(\mathbf{H} - \mathbf{H}_k + \frac{\mathbf{H}_k^2}{3\mathbf{H}}\right)$$

$\mathbf{H}_k$ is proportional to the "residual resistance" or the difference between the actual resistance observed and that which the wire would have if it were absolutely pure and free from any strain. For the wire used in this research the value of $\mathbf{H}_k$ would be large compared to the magnetic fields applied. For any given metal β should be independent of impurities and strains. It is a function of temperature only. The residual resistance may be taken as the minimum value of the resistance at low temperatures. It is interesting to note that if the data of Meissner and Scheffers for the magnetic change in resistance of gold wire at 20.4°K. are multiplied by the ratio of their

(8) (a) De Haas, de Boer and van den Berg, *Physica*, **1**, 1115 (1933–34); (b) de Haas and van den Berg, *ibid.*, **3**, 440 (1936); **4**, 8 (1937); (c) de Haas, Casimir and van den Berg, *ibid.*, **5**, 225 (1938).

(9) Meissner and Scheffers, *Physik. Z.*, **30**, 827 (1929).

(10) Kapitza, *Proc. Roy. Soc.* (London), **A123**, 292 (1929); **A126**, 683 (1930).

residual resistance to ours, the values agree with our results to within 5% below 4000 gauss. At 8000 gauss they are about 15% lower. This would be expected since their wire had a smaller value of $\mathbf{H}_k$ than ours and should deviate from the square law at smaller field strengths. The observed resistance changes differ by a factor of two.

At 4.2° the gold wire investigated by Meissner and Scheffers showed a decrease in resistance for fields less than 200 gauss and an increase for larger fields. This effect was ascribed to ferromagnetic impurities. Because of this effect and since the measurements of Meissner and Scheffers extended only to 600 gauss, it is difficult to make comparison with our results.

The single crystals of gold investigated by Meissner and Scheffers had much lower values of $\mathbf{H}_k$. It also has been found recently by Justi and Scheffers[11] that the magnetic change in resistance of single crystal gold is strongly influenced by the orientation of the magnetic field with respect to the crystal axes. For these reasons no comparison with our results has been attempted.

We thank Prof. W. F. Giauque for his advice and assistance with the measurements.

Summary

The electrical resistances of gold and silver wires have been measured at temperatures ranging from 1.5 to 20°K. and in magnetic fields from zero to 8000 gauss. For the silver wire at the lowest temperatures both the resistance and its magnetic coefficient are independent of temperature. As the temperature rises the resistance increases and the magnetic coefficient of resistance decreases. The gold wire has a minimum in resistance at about 7.7°K. The magnetic coefficient of resistance is a maximum at this temperature. The magnetic field tends to eliminate the minimum in resistance. Extrapolation of the measurements indicates that at 1°K. the magnetic coefficient would become zero and below this temperature would be negative. Such a negative coefficient of resistance has been found previously in another sample of gold wire.

(11) Justi and Scheffers, *Physik. Z.*, **37**, 383, 475 (1936).

BERKELEY, CALIF. RECEIVED NOVEMBER 2, 1938

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Rate of the Haloform Reaction. Effect of the Nature of the Halogens

BY L. H. SUTHERLAND AND J. G. ASTON

The rate of the reaction

$$CX_1X_2X_3COO^- + H_2O = CX_1X_2X_3H + HCO_3^-$$

where $X_1 = X_2 = X_3 = Br$, has been studied by DeGroote[1] at 25°, and by Fairclough[2] at several temperatures and, where $X_1 = X_2 = X_3 = Cl$, by Verhoek.[3] All found that this reaction was unimolecular with respect to the ion. The tribromo compound was studied only in water by both investigators. The trichloro was studied at several temperatures in several solvents.[3] The rate depended on the solvent but in all cases the reaction was essentially of the first order.

At 25° in water the tribromoacetate ion undergoes by far the more rapid cleavage, the cleavage of the trichloro being hardly detectable at that temperature. The energy of activation of the former was 24,100, and of the latter 36,600[3] cal. per mole.

(1) DeGroote, *Bull. soc. chim. Belg.*, **37**, 225 (1928).
(2) Fairclough, *J. Chem. Soc.*, 1186 (1938).
(3) Verhoek, THIS JOURNAL, **56**, 571 (1934).

For both practical and theoretical reasons data on the cleavage of trihaloacetic acids are desirable. In the present paper data are presented on chlorodibromoacetic acid and some preliminary data on chlorobromofluoroacetic acid. The rate of cleavage of the first of these is of the first order and depends only on the concentration of the chlorodibromoacetate ion. The average specific reaction rate constants (Col. 6) for runs with

TABLE I

HALOFORM REACTION OF SODIUM CHLORODIBROMOACETATE AT 60°

T, °C.	Starting concn. of haloacetate moles/liter	Excess NaOH moles/liter	Fraction reacted at end	Ratio hydrolysis to haloform reaction	Av. $k_1 \times 10^5$, sec.$^{-1}$
60.2	0.1210	0.0121	45	1:15	7.2
60.2	.0630	None	45	1:50	8.6
60.7	.0288	None	60	1:50	7.7
60.7	.0875	0.0088	60	1:25	7.7
60.7	.0566	.0057	60	1:25	8.6
					Av. 8.0