THERMOMAGNETIC AND GALVANOMAGNETIC EFFECTS IN ARSENIC

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Abstract

Thermomagnetic and galvanomagnetic effects—The following coefficients expressed in absolute e.m.u. are determined at 20°C in a single plate of arsenic distilled in vacuum:—specific resistance, 4.6×10^4; thermal conductivity, 3.68×10^6; Peltier heat against lead, 3.80×10^5; Thomson heat, 3.33×10^3; Hall coefficient, 4.52×10^{-2}; Nernst coefficient, 2.25×10^{-3}; Ettingshausen coefficient, 1.75×10^{-7}; Righi-Leduc coefficient, 4.15×10^{-7}. Between 0° and 170°C the temperature coefficient of resistance is 0.00435 and the thermal e.m.f. against copper is $+(7.91\,t+0.051\,t^2)\times 10^{-6}$ volts. None of these coefficients shows variation with magnetic field strength. Thermodynamic relations between different effects are checked as to order of magnitude but the difference between observed and computed values often differs by a factor of two. The thermomagnetic and galvanomagnetic effects of arsenic, antimony and bismuth show increase with atomic number; the thermal conductivity decreases. The thermal and electrical conductivity of arsenic deviates markedly from the Wiedemann-Franz ratio. When a longitudinal temperature gradient of 10°C/cm existed in the plate, a field of 8000 gauss caused a drop in temperature of 0.4°C. This temperature change is proportional to the square of both temperature gradient and field strength.

THE large values of the Hall and allied effects in bismuth and antimony suggest an investigation of these effects in arsenic, the element standing directly above them in the periodic table. This element has a further interest as its chemical properties place it in the borderland region between metals and non-metals.

The samples of arsenic used in this investigation were obtained by distilling rough crystals in vacuum at about 400°C and permitting the gaseous element which sublimes under these conditions to condense on the somewhat cooler yet still quite hot walls of the containing glass tube. The deposits thus obtained had a mirror surface on the side in contact with the glass, and a fine crystalline structure on the exposed concave side. These deposits may be removed readily from the glass and, with careful handling, ground and smoothed into rectangular plates. Although the measurements made were checked in several different specimens, those here reported were all obtained in a single plate 2.7 cm×1.1 cm ×0.02 cm. The curvature of the plate (the distilling tube was 2.3 cm in diameter) necessitates a slight correction because the magnetic field will not everywhere be normal to the surface of the plate. This correction has been applied in the results given below. The purity of the specimens is best attested by their high temperature coefficient of resistance, found to be 0.00435 per degree Centigrade. The thermo-electromotive force, likewise sensitive to small impurities, was found to be essentially the same for several different specimens. Its value measured against commercial copper between 0°C and 170°C is given by $+(7.91t+0.051t^2)\times10^{-6}$ volts. The positive sign indicating that the thermo-electric current will flow from the hot to the cold junction in the arsenic.

The magnet used in measuring the magnetic effects gave uniform fields of 4000 and 8000 gauss when excited with currents of 1 and 2 amperes respectively. The final maximum field strength was reached about 15 seconds after excitation and observations on the effects were taken one half to three quarters of a minute later. The magnet showed no appreciable heating during the measurements. For one set of measurements the pole pieces were cylindrical 3 inches in diameter, for the set recorded here the ends were tapered at 60 degrees to faces 2 inches in diameter which were covered with disks of mica. The distance between the pole pieces was always at least 1/2 inch.

The arsenic plate was mounted midway between the pole pieces in the center of the field by means of brass lugs soldered to its ends. These lugs which extended just outside the field were in turn soldered to 1/4 inch brass tubing through which water could be pumped and around which was wound a small heating coil, excited by about 0.3 amp. 60 cycle a.c. The tubes were rigidly fastened to a board 12 inches × 6 inches × 1 inch, which could be firmly clamped to the end faces of the magnet coil. The lugs which held the arsenic plate in place also served to conduct the longitudinal heat and electric currents.

Two constantan-copper couples made of wire 0.0015 inches in diameter were soldered to the center of the top and bottom edges of the plate. Additional copper wires of the same size were soldered at approximately 0.2 inch and 0.3 inch on either side of the central junction and served to measure the temperature and potential gradients. All dimensions of the plate and the distance between the couples were taken before and after the measurements by means of a carefully graduated screw and travelling microscope. The fine wires of the couple extended about an inch away from the plate at which point they were soldered to heavier wire of the same material. All thermocouple circuits were carefully insulated on hard rubber strips.

No heat insulating material came directly in contact with the arsenic plate, but the cotton packing wedged in firmly around the edges of the pole pieces prevented convective currents from causing temperature fluctuations.

All temperature and potential differences were determined by means of a potentiometer free from thermo-electric forces and a sensitive D'Arsonval galvanometer. The Hall effect was determined with both copper and constantan leads. The correction for the Ettingshausen temperature difference was negligible. The Ettingshausen effect itself was measured by noting in turn the changes in temperature of the junctions soldered to the center of the top and bottom edges of the plate. The temperature of the plate was sufficiently steady to permit of this procedure. In measuring both these effects the magnet current was turned on, reversed, and turned off and the process was repeated in the opposite direction, the reading of the potentiometer being taken after each change. The longitudinal plate current was also reversed in direction. In every case consistent readings were obtained as to sign and magnitude.

The Nernst and Righi-Leduc effects were measured in the same way except that potentiometer readings were taken only before and after reversal of the field. This modification in procedure was due to the fact that when a longitudinal temperature gradient exists in the plate, the excitation of a field causes a drop in the temperature of the plate as a whole, sufficient to mask any differential effect between the top and bottom edges due to the Nernst and Leduc effects. This temperature drop, however, is independent of the direction of the field. Hence, once the field is excited, it may be reversed without causing any general temperature change and then the differential effects between the edges become apparent. The correction for the Nernst effect on account of the Righi-Leduc temperature difference is quite appreciable and for this reason affords an independent method[1] of determining the latter effect. Determinations by the two different methods agree well and hence establish the validity of the method of using a single junction at a time in finding the Ettingshausen effect.

The thermal conductivity was measured by the "bar method"[2] and checked by direct comparison with a copper specimen of the same size by an independent method. Neither the thermal nor electrical conductivities seemed to be affected by the magnetic field. The method of determining the thermal e.m.f. was the same as previously used in this laboratory and described elsewhere.[3] It is particularly adapted to the measurement of small specimens. The Peltier and Thomson heats were computed by finding the thermal e.m.f. of the arsenic against lead using accepted

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[1] Unwin, Proc. Roy. Soc. Edin. **24**, 208 (1914).

[2] O'Day, Phys. Rev. **23**, 245 (1924).

[3] Hutchins, Am. Journ. Sci. **48**, 226 (1894).

values[4] of copper against lead and using the well known formulas. Both effects are positive indicating that heat is absorbed by the positive current from the surroundings in flowing from lead to arsenic and that heat is absorbed by the positive current in flowing from cold to hot metal. The thermal e.m.f. was not affected by the magnetic field.

The longitudinal electric current and temperature gradient were varied from 1 to 3 amperes and from 5 to 10°C/cm. The magnetic field was 4000 or 8000 gauss. Within these limits the effects showed no variation.

Table I gives the values of the effects in arsenic, measured at 20°C in absolute electromagnetic units. All effects are positive according to the usual[5] sign conventions and definitions. No attempt was made in general to determine the temperature coefficients of these effects. For purposes of comparison, the corresponding values for antimony and bismuth are included.[4,5]

TABLE I

Thermo- and galvanomagnetic effects in arsenic, antimony and bismuth

	Arsenic	Antimony	Bismuth
Specific resistance	4.60×10^{4}	4.05×10^{4}	16×10^{4}
Thermal conductivity	3.68×10^{6}	1.67×10^{6}	$.81\times10^{6}$
Peltier heat against lead	3.80×10^{5}	* $.78\times10^{5}$	-21.6×10^{5}
Thomson heat	3.33×10^{3}	*2.34×10^{3}	$.94\times10^{3}$
Hall coefficient	4.52×10^{-2}	21.9×10^{-2}	-633×10^{-2}
Nernst coefficient	2.25×10^{-3}	17.6×10^{-3}	178×10^{-3}
Ettingshausen coefficient	1.75×10^{-7}	19.4×10^{-7}	350×10^{-7}
Righi-Leduc coefficient	4.15×10^{-7}	20.1×10^{-7}	-20.5×10^{-7}

* Tables Annuelles de Constantes **2**, 351 (1913).

All corrections suggested by Hall[6] have been applied except that regarding the finite length of the plate. The fragile nature of an arsenic plate makes impracticable the development of an empirical formula showing the variation of the effects with length of plate such as Hall found in the case of gold. However, an independent investigation in the case of copper indicated that this correction for a plate of given material and thickness depended only on the ratio of length to breadth and that it was quite negligible if this ratio was greater than 2 or 3.

In magnitude the thermo- and galvanomagnetic effects in arsenic bear about the same relation to those of antimony as those of antimony do to those of bismuth. There is, then, a steady increase as one advances down this column of the periodic table. Although the effects in arsenic are smaller than in antimony and bismuth, they are much more marked than in other metals with the exception of tellurium, silicon and graphite.

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[4] Bridgman, Proc. Am. Acad. **53**, 269 (1918).

[5] Bridgman, Phys. Rev. **24**, 644 (1924).

[6] Hall, Phys. Rev. **26**, 820 (1925).

Arsenic, antimony and bismuth show a decreasing thermal conductivity in the order named. In regard to electrical conductivity, however, antimony is slightly above arsenic, so that the order is antimony, arsenic, bismuth in decreasing magnitude of electrical conductivity. The decided deviation in the case of arsenic from the Wiedemann-Franz ratio is perhaps due to its non-metallic properties. The measurement in a single specimen of all the effects affords an admirable check on the thermodynamic relations summarized by Bridgman. The observed values and those computed by these relations were always of the same order of magnitude but often differed by a factor of two.

The particular mounting of the arsenic plate used was not especially adapted to the measurement of the marked temperature drop which occurred upon excitation of the magnetic field when and only when a longitudinal temperature gradient existed in the plate. However, the writer is convinced that this reduction in temperature extends throughout the length and breadth of the plate and is neither due to a change in thermal conductivity nor to a change in the temperature of the surrounding air. This effect reached a magnitude of 0.4°C with the maximum field and gradient used. The temperature change was independent of the direction of either field of gradient and upon investigation was found to vary as the square of these quantities. Nernst is reported[7] to have observed a similar effect in copper, but the author believes that the square relation with the temperature gradient is here annunciated for the first time. It is intended to investigate this effect further to determine its relation to the dimensions of the plate. A provisional definition of its coefficient may be given, however, by the equation:

Temperature change = coefficient $(\text{temp. gradient})^2$ $(\text{field strength})^2$ The value obtained in arsenic at 20°C was -6.25×10^{-10}. The negative sign indicates a drop in temperature upon excitation of the magnetic field.

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[7] Campbell, "Galvanomagnetic and Thermomagnetic Effects," p. 254.