For $\pi/4 < \varphi < \pi/2$ they give

Condition L:

$$\pi/3 < \theta < \pi/2; \qquad (3.8a)$$

Condition R:

$$0 < \theta < \pi/4 \quad \text{and} \quad 2\pi/3 < \theta < 3\pi/4. \quad (3.8b)$$

The emitted light is left elliptically polarized in the range given by (3.7a) and (3.8a), and right elliptically polarized in the range given by (3.7b) and (3.8b). Their polarization ellipses are characterized by the values of φ which are determined as functions of θ by Eq. (3.4).

Polarization states of the other components, corresponding to the other selection rules, can be determined in the same way. The result is represented in Fig. 3 (against light). In this figure a point means that the intensity vanishes.

4. ELECTRIC AND MAGNETIC DIPOLE LINES

Polarization states of the Zeeman components of electric and magnetic dipole lines can also be determined in the same way. The result is represented in Fig. 4 (against light). In the case of the magnetic dipole lines figures are arranged according to selection rules of a magnetic quantum number M of the atom, instead of an orbital magnetic quantum number M_L.

Measurements of Thomson Coefficients for Metals at High Temperatures and of Peltier Coefficients for Solid-Liquid Interfaces of Metals

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Apparatus has been devised for measuring and measurements made of Thomson coefficients of metals at high temperatures. It is found that in the range from 400°C to the melting point the approximation $\sigma = \beta T$ is adequate for platinum, palladium, copper, and silver but not for gold, molybdenum, and tungsten.

Experimental results for the Peltier coefficients for solid-liquid interfaces of gold, silver, and copper are also reported. An experimental sensitivity of 0.1 millivolt revealed no effect in gold and silver, but $+10.2$ millivolts were obtained for copper.

I. INTRODUCTION

ALTHOUGH the thermoelectric Peltier and Thomson effects are usually of secondary importance in practical electrothermal phenomena they may become of immediate importance when thermal or electrical symmetry is a primary consideration. Thus such effects may play significant parts in contact phenomena; for example, in contact erosion and in the low frequency behavior of a circuit containing metal-semiconductor junctions. These thermoelectric effects are also of theoretical interest since they provide important clues to the electronic structure of conductors.

This article describes apparatus devised for measuring and measurements made of: (a) the liquid-solid Peltier coefficients of Au, Ag, and Cu; and (b) the Thomson coefficients for solid Pt, Pd, Ag, Au, Cu, W, and Mo at high temperatures.

II. THE LIQUID-SOLID PELTIER EFFECT OF Au, Ag, AND Cu

A. Theory

An electric current flowing through the boundary between two materials not having the same composition or structure produces heat in proportion to the current flowing. The Peltier coefficient between materials A and B at temperature T may be defined by

$$_A P_B(T) = \Delta Q / i \times t,$$

where ΔQ is the heat evolved at the junction when current i flows for time t across the junction. Here a positive sign is taken to mean that heat is absorbed by the junction when electrons flow from B to A. This is the usual convention.
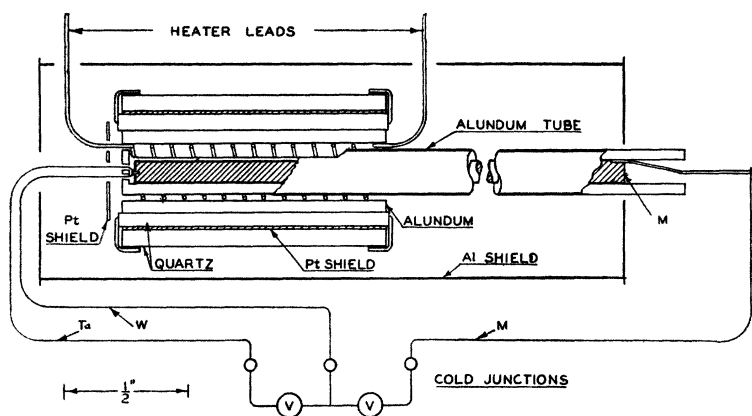
FIG. 1. Schematic diagram of apparatus for measuring the Peltier coefficient for a solid and its melt.

Pelier heat can be measured directly although its separation from Joule heat, conduction heat, radiation heat, and Thomson heat is not easy. The direct measurement of the Peltier heat between a solid melting at a high temperature and its liquid appears to be highly impractical. Therefore, we resort to an indirect method which makes use of a thermodynamic relation derived by J. J. Thomson. This relation,

$$_A P_B(T) = T _A (dE/dT)_B,$$

requires a measurement of the thermoelectric power at temperature T. If now A is a solid metal and B is its melt, the liquid-solid interface is necessarily at the melting point T_m which cannot be conveniently varied in order to obtain dE/dT. However, in a circuit containing A, its melt B, and a third material C, insoluble in both A and its melt B,

$$_A P_C(T_m) = T_{m A} (dE/dT)_C,$$

and, since the junction between A and B is at constant temperature and therefore contributes a constant voltage,

$$_B P_C(T_m) = T_{m B} (dE/dT)_C.$$

The difference of these equations is the required coefficient and is

$$_A P_B(T_m) = T_m[_A (dE/dT)_C - _B (dE/dT)_C]. \quad (1)$$

Experimentally, therefore, one obtains Peltier coefficients between the solid of interest and a third material and between the liquid of interest and the third material. The difference of these values at the melting point is the desired Peltier

coefficient between the solid and its melt. In principle, the third material can be chosen indifferently but; practically, it must meet certain experimental requirements. The method has been used by Harrison and Foote,[1] Linder,[2] Boydston,[3] and others for low melting metals. In experiments described below it has been applied to Au, Ag, and Cu. Measurements upon higher melting point metals would be much more difficult and these have not been attempted.

B. Apparatus

The apparatus sketched in Fig. 1 was constructed in order to measure Peltier coefficients for liquid-solid interfaces of higher melting metals. The specimen, a rod about 100 mils in diameter and five inches long, is mounted along the axis with one end in the furnace. A large thermal gradient runs down the specimen to the outside end where a wire of the test metal is attached. The other end of the wire acts as a cold junction. A tungsten-tantalum thermocouple made of five-mil wires is plugged into the high temperature end of the specimen. The thermocouple serves the double purpose of measuring the temperature of a small region in the specimen and measuring the thermoelectric power between either wire (actually tungsten was chosen in all experiments) and the specimen in that small region. Tests were carried out in an atmosphere of palladium-purified hydrogen flow-

[1] T. R. Harrison and P. D. Foote, J. Opt. Soc. Am. 7, 389 (1923).
[2] E. G. Linder, Phys. Rev. 29, 554 (1927).
[3] R. W. Boydston, Phys. Rev. 30, 918 (1927).

ing through the apparatus at about 2 liters per second at a pressure of about 5 mm of mercury.

The W-Ta thermocouple was calibrated against a Pt-Pt (+10 percent Rh) thermocouple. It was found that after a short anneal at a temperature higher than the experimental range, reproducible readings were obtained for the W-Ta couple and that these were fitted to better than one percent between 800 and 1400°C by the equation

$$wE_{\mathrm{Ta}}(\mu V) = 11.82(T-30) + 8.8 \times 10^{-4}(T-30)^2 - 3.5 \times 10^{-7}(T-30)^3. \quad (2)$$

Both thermocouple e.m.f. and tungsten to specimen e.m.f. were measured with a Type K potentiometer and a low resistance high sensitivity galvanometer. The over-all sensitivity was 0.1 μV.

C. Experimental Results

Representative results obtained with Ag, Au, and Cu (C.P. grade) are plotted in Fig. 2. The abscissae are voltages of the W-Ta thermocouple, transformable directly into temperatures by Eq. (2). The ordinates are voltages between M, the metal under test, and tungsten. Melting points are marked by vertical bars on the curves for gold and silver. Each test rod was cycled three times through an interval of about 150°C on each side of its melting point. The time per cycle was about two hours. The beginning of melting was best observed by an abrupt increase in efficiency of heating (due to a decrease of approximately 50 percent in the thermal conductivity of the liquid). The slopes of successive runs were very well reproduced, although occasionally an abrupt change in temperature of a fraction of a degree did occur within a run probably due to a sudden small movement of the thermocouple with respect to the test material. The slope of subsequent points always fitted the previous slope.

The curves for Ag and Au reveal no discontinuity in slope at the melting point. Since the average deviation of experimental points from a straight line over a range of about 1 millivolt and more than 100°C is about 1.0 microvolt and relative temperature is measured with a sensitivity of about 0.01°C, the sensitivity of measure of $T(dE/dT)$ is about 20 microvolts. It is concluded that the Peltier coefficients between solid

silver and its melt and between solid gold and its melt are less than 0.1 millivolt.*

A marked change of slope at the melting point was observed in the case of copper. Measurements of three cycles furnished values of (dE/dT) for solid copper equal to 13.21, 12.46, and 13.39 $\mu V/°C$, the average being 13.02 $\mu V/°C$. The corresponding measurements of (dE/dT) for liquid copper gave 3.50, 3.21, and 3.94, the average being 3.55 $\mu V/°C$. The calculated Peltier coefficient $_sP_l$ is +10.25 millivolts. The marked (greater than hundredfold) difference between copper, and silver or gold is notable in view of the marked similarities of their first order electrical properties.

III. THOMSON COEFFICIENTS FOR SOLID Pt, Pd, Ag, Au, Cu, W AND Mo AT HIGH TEMPERATURES

A. Theory

An electric current flowing in a conductor with a temperature gradient produces heat in proportion to the current flowing and to the gradient. The Thomson coefficient of a material A, in which current i flowing for time t through a
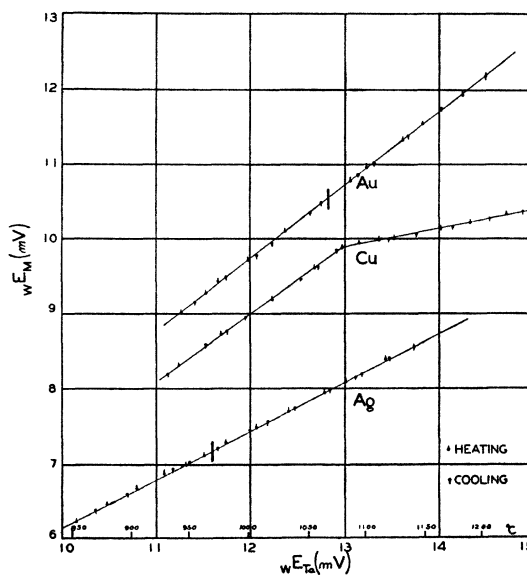

FIG. 2. Thermoelectric potentials measured in the neighborhood of melting points.

* Comparison of this value with that of potentials required to produce observed amounts of contact erosion leads to the conclusion that this effect is negligible in the erosion of gold and silver contacts.

temperature difference ΔT produces a quantity of heat ΔQ, may be defined by

$$\sigma_A(T) = \Delta Q/(\Delta T \times i \times t).$$

If heat is *evolved* as *electrons* go to places of *higher* temperature, the *positive* sign is chosen for the coefficient. This is the convention in more general usage, although opposite to that of the International Critical Tables.

In this case an indirect experimental method based on the thermodynamic relation

$$\sigma_B - \sigma_A = T_A (d^2E/dT^2)_B$$

is not feasible. Two difficulties are immediately obvious. Use of the relation to obtain a Thomson coefficient implies that one Thomson coefficient has been obtained by some other method. Moreover, an extraordinary precision of measurement would be required to obtain accurate results at high temperatures. Because of these two difficulties, the use of a direct method is indicated. More or less satisfactory direct methods have been used for low temperature measurements, but these do not appear to be readily adaptable to high temperature measurements.

In trying to measure Thomson heat directly one is of necessity also concerned with Joule heat, conduction heat, and radiation heat. Since conduction heat has the virtue of being easily measured one wants to make it large and radiation heat negligible. Therefore small surfaces and large temperature gradients are wanted. This condition is approached by heating short wires of small cross section electrically. If radiation loss is negligible, the conduction heat out an end of the wire is equal to the Joule heat plus

the Thomson heat developed between that end and the surface of maximum temperature.

In the absence of Thomson heat, the conduction heats flowing out the ends of an isotropic wire are equal if these ends are at the same temperature. Adding Thomson heat on one side and subtracting it on the other produces, in general, an asymmetric temperature condition, but one in which Thomson heat is partially compensated by a change in Joule heat produced by a readjustment of potential. It turns out, however, that the difference in heat outputs at the ends of the wire can be used as a sufficiently sensitive measure of Thomson heat.

Consider a wire with ends held at absolute temperature T_0 heated electrically to a maximum temperature T^*. Assume the wire so short that radiation loss is negligible at all values of T^* which are of interest. It will be convenient to make use of the Wiedemann-Franz law $k/\lambda = AT$, where k is thermal conductivity, λ electrical conductivity, and A a constant. Let the electrical potential at any point φ with the potential at the two ends, respectively, O and E. The heat flowing per second through the surface with zero potential and temperature T_0 is, in the steady state,

$$Q_1 = \varphi^* I + I \int_{T_0}^{T^*} \sigma dT,$$

where φ^* is the potential at T^* and I is the electrical current flowing through the wire. Through the surface at potential E and temperature T_0 the heat flowing per second is

$$Q_2 = (E - \varphi^*) I - I \int_{T_0}^{T^*} \sigma dT.$$

The difference between these divided by the total heat output is

$$(Q_1 - Q_2)/(Q_1 + Q_2) = \Delta Q/Q = [(2\varphi^* - E)/E]$$

$$+ (2/E) \int_{T_0}^{T^*} \sigma dT. \quad (3)$$

One sees that φ^* must be evaluated if σ is to be obtained from experimental measurements of $\Delta Q/Q$ as a function of E and T^*.

Neglecting the Thomson effect, the differential

TABLE I.

T^* °K	a	b	c	d
400	0.1712	0.1458	0.1248	0.1076
500	0.2796	0.2133	0.1607	0.1326
600	0.3546	0.2500	0.1824	0.1375
700	0.4099	0.2722	0.1937	0.1388
800	0.4524	0.2864	0.1946	0.1386
1000	0.5137	0.3033	0.1967	0.1376
1200	0.5558	0.3124	0.1976	0.1365
1400	0.5862	0.3179	0.1977	0.1360
1600	0.6096	0.3216	0.1977	0.1355
1800	0.6284	0.3240	0.1976	0.1351
2000	0.6432	0.3256	0.1974	0.1348
2200	0.6550	0.3271	0.1974	0.1344
2400	0.6660	0.3281	0.1973	0.1340
2600	0.6748	0.3289	0.1972	0.1336

FIG. 3. Schematic diagram of apparatus for measuring Thomsom coefficients at high temperatures.

WATER

CURRENT LEADS

WATER

CURRENT LEADS

THERMOCOUPLES

TEST METAL

V

l'
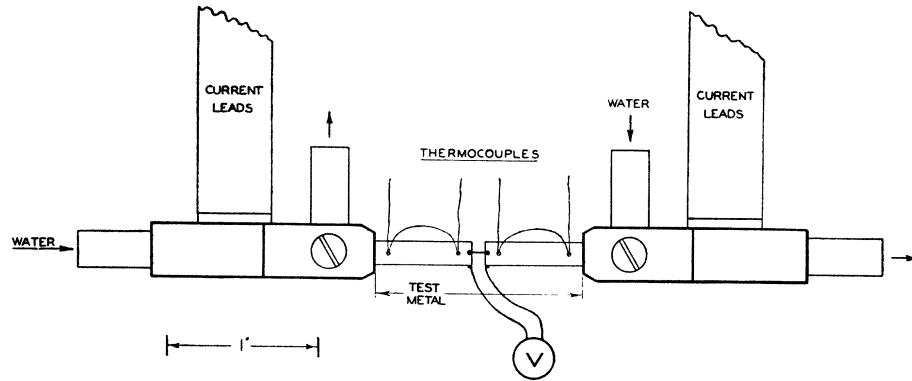
equations to be satisfied are

$$\nabla \cdot k\nabla T + \lambda(\nabla\varphi)^2 = 0, \quad \nabla \cdot \lambda\nabla\varphi = 0,$$

which may be written in the single equation

$$\nabla(\lambda\varphi\nabla\varphi + k\nabla T) = 0. \qquad (4)$$

This equation determines a relation $T = f(\varphi)$ uniquely under conditions general enough to include our problem.[4] The solution under the prescribed conditions is

$$\int_{T_0}^{T} (k/\lambda)dT = A \int_{T_0}^{T} TdT = \int_{0}^{\varphi} (\varphi^* - \varphi)d\varphi. \qquad (5)$$

Taking Thomson heat into consideration, the term $\sigma\lambda\nabla\varphi \cdot \nabla T$ is added to the left of Eq. (4) and the solution becomes

$$A \int_{T_0}^{T} TdT = \int_{0}^{\varphi}\left[(\varphi^* - \varphi) + \int_{T(\varphi)}^{T} \sigma dT\right]d\varphi.$$

On the low potential side of T^*

$$A \int_{T_0}^{T^*} TdT = \int_{0}^{\varphi^*}\left[(\varphi^* - \varphi) + \int_{T}^{T^*} \sigma dT\right]d\varphi,$$

and on the high potential side

$$A \int_{T_0}^{T^*} TdT = \int_{E}^{\varphi^*}\left[(\varphi^* - \varphi) + \int_{T}^{T^*} \sigma dT\right]d\varphi.$$

Subtracting, obtain

$$(E/2)(E - 2\varphi^*) = \int_{0}^{\varphi^*} d\varphi \int_{T}^{T^*} \sigma dT$$

$$- \int_{E}^{\varphi^*} d\varphi \int_{T}^{T^*} \sigma dT. \qquad (6)$$

In general, σ is small and produces a small perturbation of the symmetric function $T = f(\varphi)$ of Eq. (5). Therefore the integrals on the right of Eq. (6) can be evaluated by integrating to the average limit $E/2$ over the path

$$d\varphi = [(AT)^{\frac{1}{2}}/(T^{*2} - T^2)^{\frac{1}{2}}]dT$$

obtained from (4). This yields

$$(2\varphi^* - E)/E = -[4(A)^{\frac{1}{2}}/E^2]$$

$$\times \int_{T}^{T^*} d(T^{*2} - T^2)^{\frac{1}{2}} \int_{T}^{T^*} \sigma dT, \qquad (7)$$

the quantity needed in Eq. (3). After substituting (7) in (3), integrating by parts, and substitution of $E = 2(A)^{\frac{1}{2}}(T^{*2} - T_0^2)^{\frac{1}{2}}$ from Eq. (5) one obtains the relation

$$(\Delta Q/Q)(E/2)$$

$$= [1/(T^{*2} - T_0^2)^{\frac{1}{2}}] \int_{T_0}^{T^*} \sigma(T^{*2} - T^2)^{\frac{1}{2}}dT.$$

This is simply evaluated if σ is proportional to the temperature, but unfortunately this assumption is not justified in general. Represent σ by a power series, $\sigma = \alpha + \beta T + \gamma T^2 + \cdots$. It is then found[5] that

$$(\Delta Q/Q)(E/2) = \alpha a T^* + \beta b T^{*2}$$
$$+ \gamma c T^{*3} + \delta d T^{*4} + \cdots \qquad (8)$$

---

[4] Two excellent papers concerned with relations between potential and temperature in steady-state problems and in which the mathematical foundations for the above analysis

is given detailed attention are: F. Kohlrausch, Ann. d. Physik 1, 132 (1900) and H. Diesselhorst, Ann. d. Physik 1, 312 (1900).
[5] Alternatively the experimental values of $(\Delta Q/Q)(E/2)$ may be expressed as a power series and the integral equation solved for σ. The equation has been reduced to Abel's form and solved by J. M. Richardson.

where

$$a = \tfrac{1}{2}[[((\pi/2) - \sin^{-1}r)/(1 - r^2)^{\frac{1}{2}}] - r],$$
$$b = \tfrac{1}{3}[1 - r^2],$$
$$c = \tfrac{1}{4}[[((\pi/2) - \sin^{-1}r)/2(1 - r^2)^{\frac{1}{2}}] + r(\tfrac{1}{2} - r^2)],$$
$$d = \tfrac{1}{5}[1 - r^2][r^2 + \tfrac{2}{3}],$$

in which $r = T_0/T^*$. Values for these factors with T_0 equal to 300°K are given in Table I.

If the experimental metal obeys the Wiedemann-Franz Law well, T^* is obtained from (5) and the observed potential difference E. For small σ the accuracy of the method should then be limited only by experimental accuracy. Actually, the law has been found to be well obeyed by Ag, Au, Cu, Pt, and Pd. In the case of W and Mo, the law seemed well enough obeyed to permit substitution of pyrometrically observed values of T^*. This amounts to choosing an average value of A different for each T^*.

A theoretical sensitivity for the method can be calculated by comparing $\Delta Q/Q$ with the Thomson heat contribution to $\Delta Q/Q$. The ratio of these quantities,

$$\frac{\alpha a T^* + \beta b T^{*2} + \gamma c T^{*3} + \cdots}{\alpha(T^* - T_0) + (\beta/2)(T^{*2} - T_0^2) + (\gamma/3)(T^{*3} - T_0^3) + \cdots},$$

is about $\tfrac{2}{3}$ if $\sigma = \alpha$, $\tfrac{2}{3}$ if $\sigma = \beta T$, and about 6/10 if $\sigma = \gamma T^2$. Thus the compensating shift in potential does not seriously reduce the sensitivity of $\Delta Q/Q$ to the Thomson heat evolved. If this compensating shift in potential had very greatly reduced the sensitivity, a better experimental method would have been to measure this po-

tential shift by means of a probe electrode attached to the center of the test metal.

B. Apparatus

A diagram of the experimental apparatus is given in Fig. 3. The test material, which is heated electrically to the maximum temperature
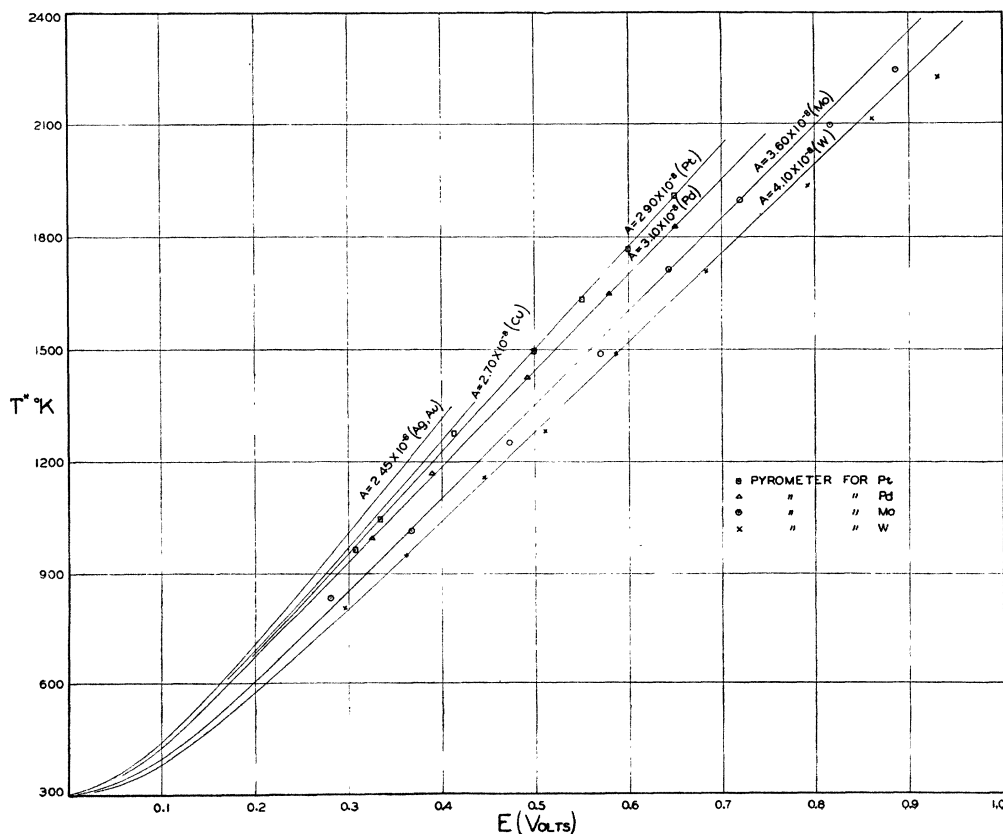

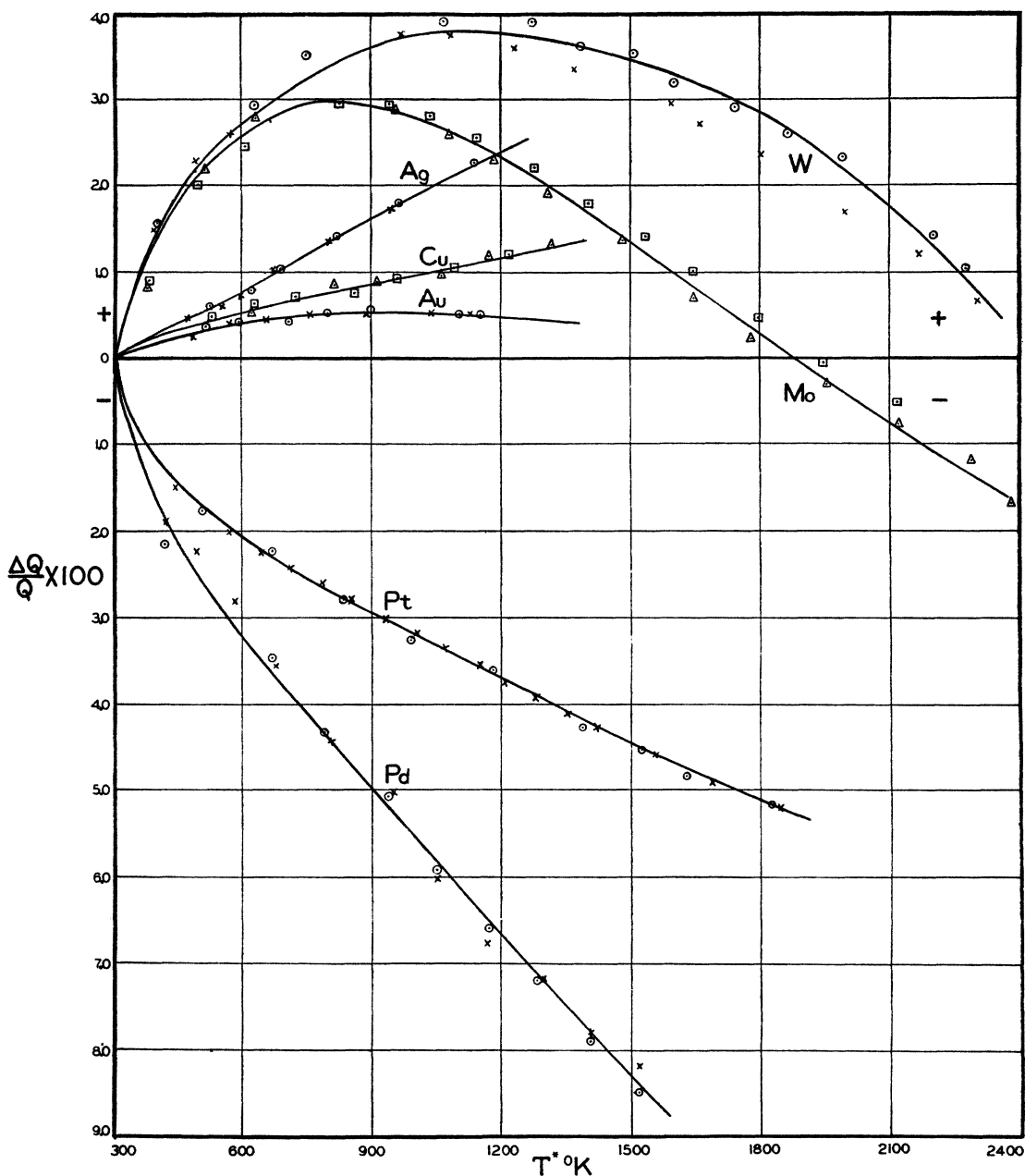FIG. 4. Temperature vs. voltage data.

FIG. 5. Experimental values of $(\Delta Q/Q) \times 100$ plotted against temperature.

T^*, is the small wire at the center. In order to measure heat output easily, the ends of this wire are beaded and welded to bars of the same metal. Beading and welding insure good thermal and electrical contact. The bars are made of the test metal to eliminate Peltier heating at the welds. The design is such that the temperature rise in the bars was approximately 2° per 100°

maximum temperature rise. Temperature gradients in the bars were measured by Chromel-Alumel couples of 5-mil wire coated with 5 mils of glass and set with silver paste in 30-mil holes at the ends of the bars. The electrical resistance between bars and thermocouples was 10^8 ohms or more. The two couples of one bar were connected in opposition, and the resulting potential

measured with a potentiometer and galvanometer sensitive to 0.1 μv. Thus the differential temperature was measured with a sensitivity of about 0.002°C. To maintain the temperature T_0 at the far ends of the bars, they were set firmly in the large copper clamps, the important feature of which is fast internal flow of thermostated water. To obtain the maximum accuracy it is essential only that the ends of the rods be held at constant temperature for about one minute, which is the time required to make a measurement of $\Delta Q/Q$.

The limiting ratio of the length l of test wire to its diameter d which insures that the ratio of radiation loss Q_r to conduction loss Q_c will be less than a prescribed amount was calculated, in the case of copper, from the formula $Q_r/Q_c \simeq T^{*3}l^2 \times 2 \times 10^{-12}/d$. Allowing a maximum radiation loss of 2 percent at 1000°C $l^2/d \simeq 10$ so that a 0.02-cm wire can be about 0.4 cm in length. On the other hand a 0.02-cm molybdenum wire (with thermal conductivity about one-third that of copper) at 2500°C can be no more than about 0.06 cm long. An experimental check on radiation loss was made in all tests by measuring current. The measure of the electrical heat generated can then be compared with the measure of the total conduction loss and this ratio must remain constant with increasing T^*. In no case in the data

given below did the ratio change by more than 3 percent. In a few cases reduction of the data to absolute amounts was made. Agreement to better than one percent at high temperatures proved convection losses to be negligible.

The potential E was measured at the ends of the rods by attached wires of the test metal connected through a switch to the potentiometer. The potential was supplied by a number of storage batteries in series connected to the clamps through a reversing switch and an adjustable low resistance. Currents up to a maximum of about thirty amperes were required with test wires ranging from 6 to 10 mils in diameter.

The change in thermal conductivity in the rods amounted at most to about 1 percent. Therefore the potentiometer reading alone is a sufficient measure of the heat flow through the rod if the termocouple in the high temperature end of the rod does not lag badly with increasing temperature. A small lag (e.g., 5 percent at the highest temperature) does not interfere seriously with the measurement of a small $\Delta Q/Q$. In separate measurements the maximum lag found was much less than 5 percent.

In order to obtain the difference in heats flowing through the rods, the like pair of thermocouple wires from one rod were connected in
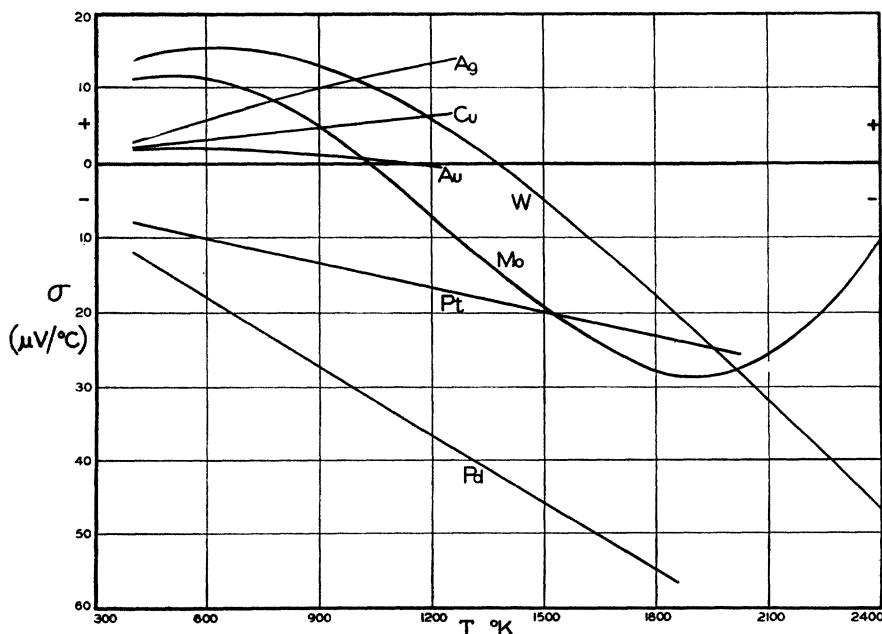

Fig. 6. Calculated Thomson coefficients.

opposition to the like pair from the other, the difference measured, then measured again with the current reversed. The difference of these differences is twice the required ΔQ and this procedure automatically corrects for unavoidable small asymmetry.

Ag, Au, Pt, and Pd were measured in air. Cu, Mo, and W were measured in hydrogen, and this was done simply by fitting a small glass tube over the wire around the ends of the rods and providing the glass tube with hydrogen input and output tubes. The flow of hydrogen was made slow to avoid convection losses.

C. Experimental Results

The dependence of T^* on E is given by $E = 2(A)^{\frac{1}{2}}(T^{*2} - T_0^2)^{\frac{1}{2}}$ if the Wiedemann-Franz law holds. Variation in A of the order of ten percent produces a variation of five percent in T^* and can be tolerated if great accuracy is not sought. Experimental data in the literature confirm the constancy of A within this limit in the case of Au, Ag, and Cu. Observation of the voltage which just melts a wire is available as an experimental check. It was found that Au wires melt at 0.410 volt, Ag wires at 0.365 volt, and Cu wires at 0.435 volt. Combining these values with data in the literature, $A_{Ag} = A_{Au}$ was chosen equal to 2.45×10^{-8} watt ohm/(deg.) and A_{Cu} equal to 2.70×10^{-8}. Pt, Pd, Mo, and W do not obey the Wiedemann-Franz law so well. Therefore, pyrometric observations of T^* were made for these metals and the results are plotted against voltage in Fig. 4. The data for Pt fit a curve with A equal to 2.90×10^{-8} and this value is confirmed by the observed melting voltage equal to 0.690. The data for Pd fit a curve with A equal to 3.10×10^{-8} and this value is confirmed by the observed melting voltage equal to 0.645. Pyrometric data for Mo are well fitted below 2000°K by the curve with A equal to 3.60×10^{-8} and W below 2000°K by the curve with A equal to 4.10×10^{-8}. The value for Mo is somewhat higher than data in the literature would lead one to expect. Above 2000°K, T^* for these two metals was weighted in favor of the pyrometric data. The W and Mo wires used did not melt without significant radiation loss, and therefore their melting voltages are not recorded. The corresponding curves for Ag, Au,

TABLE II.

Metal	$\alpha \times 10^6$	$\beta \times 10^8$	$\gamma \times 10^{10}$	$\delta \times 10^{14}$
Au	+0.454	+0.507	-4.95	——
Ag	-4.21	+1.868	-3.45	——
Cu	-0.29	+0.544	——	——
Pt	-3.66	-1.083	——	——
Pd	——	-3.03	——	——
Mo	-7.96	+8.46	-1.042	+2.86
W	——	+5.19	-0.486	+0.792

and Cu, as determined by the method described, are drawn here also for the purpose of comparison. Below the lower limit of the pyrometric observations (about 800°K) the values of A for Pt, Pd, Mo, and W continue to decrease with decreasing temperature so that, in using the fixed values of A indicated, one is effectively using an A which is averaged for the range from 800° to 2000°K. Data for Mo and W are probably more seriously affected by this treatment than are those for Pt and Pd. One observes also in Fig. 4 considerable deviation of experimental values from the averaged curves for W and Mo above 2000°K.

Observed values of $\Delta Q/Q$ are plotted against T^* in Fig. 5. T^* has been obtained from Fig. 4 and the observed voltage E. The results of two runs are plotted in each case, and except for Mo and W, these check each other very well. No systematic search for the cause of Mo and W variations was made, but it was found that the results of a second run with the same wire (therefore with a well annealed wire) agreed with the results of the first run.

The curves drawn in Fig. 5 were obtained from Eq. (3) using values of α, β, γ, and δ given in Table II.** The Thomson coefficients calculated from these values of α, β, γ, and δ are plotted against temperature in Fig. 6.***

D. Discussion

With the apparatus described $\Delta Q/Q$ is measured with a sensitivity of the order of 10 percent per 100°C rise in temperature, the sensitivity

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** Values for directly observed Thomson coefficients given in the I.C.T. are given in the same form but with opposite sign and for different temperature intervals.
*** The large negative values obtained for platinum and palladium, if representative of values for the liquid metals, lead to the conclusion that under some conditions Thompson heat may be a significant source of erosion in platinum and palladium contacts.

being lowest for Au and highest for Pd. As the temperature span of measurement increases the accuracy of measurement of $\Delta Q/Q$ for this span increases, thus average values are obtained with accuracy for a sufficiently wide temperature range. The method is obviously not sensitive to abrupt changes in the Thomson coefficient such as might result, for example, from a phase transition. Similarly, the average values assigned to the ends of the range of measurement are not well determined.

There are few high temperature data for Thomson coefficients available in the literature and extrapolated low temperature values do not agree, in general, with the results reported above. Thus Berg[6] finds σ_{Pt} numerically decreasing with increasing temperature in the range 0°C to 128°C. Borelius and Gunneson[7] find σ_{Au} increasing with increasing temperature in the range 0°C to 300°C, but Lecher[8] reports values for Cu and Ag which have the same trend as the values reported above although about half as large in the neighborhood of 300°C. Fair agreement with the literature is obtained by extrapolation of the above results to 0°C. Worthing[9] reports σ_W increasing numerically from -10 at 1500°K to -35 at 2200°K, and these values are in fair agreement with those found here.

The high temperature reversal found for σ_{Mo} (Fig. 6) may be exaggerated due both to reduction in accuracy at the ends of the region of measurement and to a failure to determine and use a more accurate temperature-voltage relation. The data for $\Delta Q/Q$ strongly indicate an inflection point at about 2000°K and this produces zero slope of $d\sigma dT$ in this neighborhood. A more accurate study of this metal is, however, required before the sharp reversal reported can be accepted confidently. The curve for W above 2000°K does not excite suspicion, but is subject to the same sort of error.

It is to be noticed that Pt, Pd, Cu and Ag confirm the theoretical prediction that to a first approximation σ should be proportional to the absolute temperature, and that either sign is possible.[10] Negative values are reported in the case of Pt and Pd, and positive values in the case of Cu and Ag. More complicated behavior is observed with Au, Mo, and W. In the case of Au, however, σ is comparatively small. Thus at higher temperatures Au should be used to replace Pb when using the method of measuring σ based on the thermodynamic equation.

ACKNOWLEDGMENT

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