DETERMINATION OF PELTIER ELECTROMOTIVE FORCE FOR SEVERAL METALS BY COMPENSATION METHODS.

By A. E. Caswell.

Introductory Note.—The great discrepancies between the values of the Peltier electromotive force between various metals obtained by different investigators, and especially between the values of Le Roux[1] and Jahn,[2] suggested the advisability of devising a new method of measurement not open to the objections which may be brought against the methods previously employed, and by such method redetermining the Peltier electromotive force for a number of combinations. The development of the thermo-electric and electron theories renders trustworthy determinations of this quantity more important than heretofore. Accordingly, upon the suggestion of Professor Fernando Sanford, the present work was undertaken, and throughout the writer has profited by his timely advice and suggestions as well as that of other members of the department.

Historical Sketch.

Discovery.—Peltier[3] was the first to discover that if a current be sent across the junction of two dissimilar metals there will be either an evolution or absorption of heat at the junction, and if the direction of the current be reversed the effect is also reversed. In other words, the junction of two dissimilar metals is the seat of an electromotive force. Its magnitude cannot be measured directly, so one must resort to the expedient of determining the amount of heat associated with the passage of a given quantity of electricity across the junction, or else deduce its value from more or less doubtful considerations.

Thomson's Theorem.—Through an application of the dynamical theory of heat to thermo-electric phenomena Sir William Thomson (Lord Kelvin) came to the conclusion that, if P = Peltier E.M.F., E = thermo E.M.F., T = absolute temperature, then $P = T\dfrac{dE}{dT}$.[4] The same considerations led him to the conclusion that a similar effect should

[1] Le Roux, Ann. Chim. Phys., IV., 10, pp. 201–291, 1867.

[2] Jahn, Pogg. Ann., N. F., 34, pp. 755–785, 1888.

[3] Peltier, Ann. Chim. Phys., II., 56, pp. 371–386, 1834.

[4] Kelvin, Lord, Math. and Phys. Papers, pp. 232–291, 1882; also Trans. Roy. Soc. Edinburgh, 1854.

exist between unequally heated portions of the same metal. The latter phenomenon was afterward discovered and is known as the Thomson effect. This discovery would seem to verify Thomson's conclusions. If we accept this equation two results follow: (1) knowing the way in in which the thermo E.M.F. varies at any temperature or its value for a very small range of temperature including the desired temperature, we may compute the value of the Peltier E.M.F. for that temperature; and (2) the value of the Peltier E.M.F. at the neutral temperature must be zero. From (1) it follows that at any given temperature the ratio of the Peltier E.M.F. to the thermo E.M.F. for any two metals should be constant and equal to the temperature (absolute). This point has been tested by most experimenters on the Peltier E.M.F. but the results in a number of cases have only been given in relative units. The second result has also been investigated. All the results of experiment seem to justify this equation in a general way.

Direct Determinations.—The direct determination of the amount of heat associated with the passage of a known quantity of electricity across a metallic junction was carried out by Le Roux who worked with copper against several other metals, notably bismuth. Bismuth bars were welded together into the form of a horse-shoe and to the ends heavy strips of copper were soldered. The junctions were immersed in rather crude calorimeters containing water. Current was sent for fifteen minutes in each direction and corresponding temperature changes in each calorimeter observed by means of mercury thermometers. In the copper-bismuth case the Joule heat was about four times the Peltier heat.

Edlund[1] obtained relative values for the Peltier E.M.F. by means of junctions inclosed in two nickel-plated copper tubes forming the two bulbs of a differential air thermometer. For comparison he also measured the thermo E.M.F. The electromotive force was determined by a sensitive galvanometer and the temperatures by two sensitive mercury thermometers. Assuming that his results for aluminium are the same as those which I have obtained I have computed his values of the Peltier E.M.F. and of the thermo E.M.F. These values are given in the following table. They probably do not differ from his true values by more than ten per cent. The computed values are expressed in millivolts.

Sundell,[2] working with Edlund's apparatus made similar measurements on antimony-bismuth alloys against copper, also on the bismuth used by Edlund. His value for copper-bismuth differed from that obtained by Edlund. This he attributed to some change in the crystalline structure of the bismuth.

[1] Edlund, Pogg. Ann., *143*, pp. 404–428, and 534–568, 1871; also *140*, pp. 435–450, 1870.
[2] Sundell, Pogg. Ann., *149*, pp. 144–170, 1873.

Jahn determined the Peltier heat by immersing one junction of a couple in a Bunsen ice calorimeter. Current was sent in both directions and the corresponding quantities of heat determined. From these measurements the Peltier heat was calculated. Jahn's results refer to 0° C., and apparently are accurate to within two or three per cent. In order to test the truth of Thomson's theorem Klemenĉiĉ measured the thermo E.M.F. of the couples used by Jahn. His results, multiplied by 273, the absolute temperature of Jahn's experiments, together with those of Jahn are shown in Table IX.

TABLE I.

Edlund's Probable Values.

Metal Used Against Copper.	Peltier E.M.F.		Thermo E.M.F. $\times$ 289.	
	Relative.	Computed.	Relative.	Computed.
—				
Iron..............	130.99	2.96	146.18	3.08
Cadmium.........	6.88	.155	9.79	.206
Zinc.............	.34	.008	.76	.016
Copper...........	——	——	——	——
Silver...........	1.29	.029	1.89	.040
Gold.............	14.76	.334	23.92	.505
Lead.............	22.20	.502	27.27	.575
Tin..............	24.71	.558	38.84	.82
Aluminium	30.77	.695	42.15	.89
Platinum.........	45.03	1.017	58.41	1.23
Palladium........	96.23	2.175	115.04	2.43
Bismuth..........	783.1	17.70	835.1	17.62
+				

Cermak,[1] using Lecher's[2] thermo-electric calorimeter, has measured the Peltier effect for couples of constantan against iron, lead, tin, cadmium and mercury, and for a copper-nickel couple, over wide ranges of temperature. His results for the copper-nickel couple are as follows:

Temperatures..............19 95 235 290 340 445
Gram-calories $\times$ 10³........ 1.92 2.15 2.45 2.06 1.01 2.38

The result for 19° C. gives $P = 8.04$ millivolts. He has also found that there is no change either of the Peltier E.M.F. or thermo E.M.F. as the metals change from the solid to the liquid state, or vice versa.

Barker,[3] using the first of the methods employed in the present investigation which he independently devised, has measured the Peltier E.M.F.

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[1] Cermak, Ann. d. Physik, *24*, 2, pp. 351–356, 1907; also *26*, 3, pp. 521–531, 1908. Also in Akad. Wiss. Wien, Sitz. Ber., 116, *2a*, pp. 657–668, 1907.

[2] Lecher, Wiener Ber., 115, *2a*, p. 1506, 1906.

[3] Barker, PHYS. REV., XXXI., p. 321, Oct., 1910.

for a copper-nickel couple and found it to be 6.75 millivolts at 28°.7 C.

The remainder of the work which has been done upon the subject is qualitative rather than quantitative. The values obtained are comparative and cannot be reduced to absolute units. The method used by Peltier himself was to solder two metals bars together in the form of a cross, connect two adjacent extremities to a galvanometer and the other two to a source of current. Current was then sent first in one direction for a given length of time and then in the opposite direction, and the corresponding changes in the galvanometer deflection noted. From these data one might arrange the metals in a Peltier series without giving the actual values of the E.M.F. between any pair. This method has been frequently used. Another common method is to make a thermo-electric couple of the pair of metals to be investigated, and arrange connections so that it may be quickly connected either to a source of current or a galvanometer. Current is sent through the couple thereby heating one junction and cooling the other. The circuit is then broken and the couple connected with the galvanometer. The galvanometer deflection may be used to compute the difference in temperature. For a given current this difference should be approximately proportional to the Peltier E.M.F.

Lenz[1] bored a small hole in the junction of two coaxial bars of bismuth and antimony. This he filled with water and cooled the whole apparatus to 0° C. Then by sending a current across the junction from bismuth to antimony he was able, not only to freeze the water in the hole, but also, to cool the ice to − 4°.5 C.

Proportional to Current.—Icilius,[2] using a thermopile consisting of 32 bismuth-antimony couples, found that the heating or cooling of the junctions was proportional to the strength of the current sent across them. Frankenheim[3] confirmed this result by using Peltier crosses of bismuth-copper, copper-iron, bismuth-antimony, and iron-German-silver.

Zero at the Neutral Point.—Budde[4] investigated the question regarding the value of the Peltier effect at the thermo-electric neutral point for copper-iron and zinc-silver couples. In the latter case the thermo E.M.F. was too small for him to get any satisfactory results. Using the second of the qualitative methods mentioned above he found the Peltier effect to be zero at 240° C. and the thermo E.M.F. zero at 270° C. for the copper-iron couple. This he considered a sufficient agreement. In a

[1] Lenz, Pogg. Ann., *44*, p. 342, 1838.
[2] Icilius, Pogg. Ann., *89*, p. 377, 1853.
[3] Frankenheim, Pogg. Ann., *91*, p. 161, 1854.
[4] Budde, Pogg. Ann., *153*, pp. 343–372, 1874.

similar way Battelli[1] investigated the Peltier effect and thermo E.M.F. for lead against (1) an alloy of 10 parts antimony to 1 part tin, and (2) an alloy of 18 parts tin to 1 part cadmium. For the thermo E.M.F. he found the neutral points to be 12° C. and 16° C., respectively. The Peltier effect was zero at 16° C. and 31°.5 C. Believing that the experiments of Budde and Battelli by no means prove that the Peltier effect is zero at the neutral point, La Rosa[2] investigated the point very carefully. To the ends of a bar of pure zinc bent into the form of a V, he soldered iron and platinum wires. The iron wires were connected to the galvanometer, and current sent through the platinum-zinc junctions. Readings were taken from 19° C. to 46°.5 C., the neutral point being found at 36°.6 C. The curve for temperatures as abscissæ and galvanometer deflections as ordinates cut the temperature axis slightly above 36°.5 C. Therefore the Peltier effect becomes zero at the neutral point within the limits of experimental error.

Agreement with Thermo-electric Diagram.—Campbell,[3] using couples consisting of a U-shaped piece of lead or other metal soldered to iron blocks, obtained results which appear to agree with the thermo-electric diagram given in Tait's manual on "Heat." The temperature differences of his junctions were measured by means of an iron-German-silver thermo-couple, separated from the junctions by several thicknesses of paper. Gore[4] obtained similar results using a thermopile, consisting of 36 bismuth-antimony couples, heated in a hot-water jacketed chamber from 9° to 85° C. With Peltier crosses he also found that the Peltier effect increased with temperature for iron-German-silver, bismuth-antimony, and bismuth-silver. For antimony-silver it seemed constant.

Variation with Temperature.—By means of Thomson's equation, $P = T\dfrac{dE}{dT}$, Harrison[5] has found the value of the Peltier E.M.F. at the temperature of liquid air (− 191°.2 C.). His results are:

$$\begin{array}{ll} \text{Copper-iron} \dotfill & 1{,}156 \text{ microvolts,} \\ \text{Copper-nickel} \dotfill & 7{,}697 \text{ microvolts.} \end{array}$$

Bausenwein[6] has found that, for the iron-constantan couple which he used, both the thermo E.M.F. and the Peltier E.M.F. increase in a

[1] Battelli, R. Acc. dei Lincei (1) Rendic., *3*, pp. 404–407, 1887, also Beibl., *11*, 726, 1887.
[2] LaRosa, Acc. Lincei, Atti, *13*, pp. 167–173, 1904; also Sc. Abs., *7*, 2968.
[3] Campbell, Proc. Roy. Soc. Edinburgh, *11*, 807, 1882–3; also Beibl., *8*, p. 231, 1884.
[4] Gore, Phil. Mag. 3, *21*, pp. 351–362, 1886.
[5] Harrison, Phil. Mag., 6, *3*, pp. 177–195, 1902.
[6] Bausenwein, Akad. Wiss. Wien, Sitz. Ber., *144*, 2a, pp. 1625–1633, 1905; also Sc. Abs., *9*, 1110.

linear manner with the temperature (absolute). But the Peltier effect
is not proportional to the absolute temperature, its curve cutting the
axis of temperatures at −600° C. Hence this combination does not
obey Thomson's law. His experiments extended over the interval from
0° C. to 800° C. Rzika[1] carried out similar measurements on a couple
made from the same metals and obtained contradictory results. The
principal source of error is probably due to changes in the specific heats
at high temperatures, which changes are not known. The question of
variation with temperature is still unsettled.

Theories.—In addition to Sir William Thomson's theoretical work on
thermo-electricity, two recent developments are of interest. The
first is the explanation of the Peltier effect upon the basis of the electron
theory,[2] the second is due to Lecher.[3]

Electron Theory.—In the electron theory it is assumed that the con-
centration of the electrons in any two metals is, in general, different for
the same temperature. If, then, two metals are placed in contact, the
electrons will diffuse from that metal in which the concentration is large
to that in which it is small. This diffusion will continue until the electric
field set up by the motion of the electrons away from their compensating
positive charges is sufficient to balance the difference of pressure due to
the difference of concentration. The resulting potential difference,
assumed to be identical with the Peltier E.M.F., is given by the equation

$P = \dfrac{4\alpha T}{3\epsilon} \log \dfrac{N_1}{N_2}$, where N_1, N_2 are the concentrations of the electrons

in the two metals, αT is the mean kinetic energy of an electron, and ϵ is
the charge on an electron. From other considerations N is found to be
proportional to the inverse of the square root of the absolute temperature.
Hence N_1/N_2 is constant. The Peltier E.M.F. should, therefore, be strictly
proportional to the absolute temperature, and so could not be zero at the
neutral point unless it were zero at all temperatures. This seems to be
contrary to the facts.

Lecher's Diagram—Lecher obtains the Peltier heat by superimposing
upon a diagram representing the Thomson heat for the two metals
concerned, a curve representing the energy of the thermo E.M.F. between
the two metals. In this way he finds the Peltier effect between iron
and silver to be 7.3×10^{-4} gram-calories per coulomb, or 3.06 millivolts.
This agrees well with experiment as may be seen by referring to Table IX.

[1] Rzika, Akad. Wiss. Wien, Sitz. Ber., *116, 2a*, pp. 715–722, 1907; also Science Abs., *11*, 26.
[2] Drude, Ann. d. Physik, 4, *1*, p. 566, 1900, and 4, *3*, p. 369, 1900.
[3] Lecher, Ann. d. Physik, 4, *20*, pp. 480–502, 1906.

METHODS OF MEASUREMENT.

Two methods of measurement were devised, both of which depend upon maintaining both junctions of the given couple at the same temperature by supplying heat at the junction where cooling is taking place. This precludes the possibility of error arising out of other thermo-electric effects. The Peltier electromotive force is determined by measuring the ratio of the heat so supplied to the quantity of electricity sent across the junction. The first method, as previously stated, has also been devised by Barker and by him employed in the measurement of the Peltier E.M.F. in a copper-nickel junction. In view of the fact that measurements were already being made by this method when his article was published, also that he had not investigated the method completely and intimated that he had discontinued the work, it was decided to proceed. The discussion of the method and the mathematical calculations here given are fuller than those in his article, and so may justify such repetitions as occur.

FIRST, OR SEPARATE HEATING-COIL, METHOD.

This consists essentially in placing the two junctions of the couple in two separate calorimeters containing equal quantities of a suitable liquid. Each is provided with an electric heating-coil of known resistance, by means of which sufficient heat is supplied to the liquid where cooling is taking place to maintain it at the same temperature as that where heat is evolved, the equality of temperature being shown by a differential thermometer.

Two Dewar silvered glass vacuum flasks (inside dimensions: diameter 3.1 cm., depth 15 cm.) were used as calorimeters because they are the best heat insulators available and their heat capacity is small. These were held upright in a wooden box. The couples were made from heavy strips of the metals and were in the form of a double U, the junctions being at the bottoms of the U's.

Apparatus.—Three different forms of heating-coil were tried. The first coils, used only with the gas stirrers mentioned below, consisted of a considerable length of manganin wire doubled and then kinked as shown in Fig. 1. These were placed in the center of the U and extended upward to the surface of the liquid. This form was discarded because the coils occupied too much space. Coils of 65 cm. of German-silver resistance wire were then made. The wire was wound around a celluloid hoop, the perimeter of which was 6.5 cm. and depth 2.5 cm. The manner of winding is shown in Fig. 2. The hoop was placed in the

center of the U with its axis vertical, and the stirrer and one junction of
the thermo-element, used as a thermometer, were placed within it. The
resistance of these coils was 3.057 and 3.072 ohms, respectively. This
arrangement was abandoned because the hoop, by impeding the circu-
lation of the liquid, lengthened the time elapsing before a steady temper-
ature condition could be set up. The arrangement finally adopted was
similar to the first except that the wire was crowded into small space
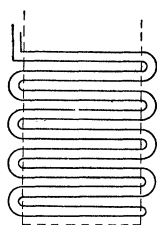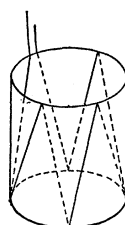and placed in the bottom of the U as shown in Fig. 3. The length of
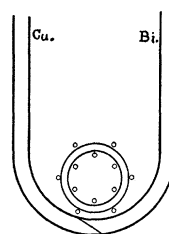

Fig. 1.   Fig. 2.   Fig. 3.

the coils so formed was 2.5 cm., so that they extended across the calo-
rimeters. In this way heat was supplied very close to the place where it
was being absorbed, and the coil, while being small, permitted free
circulation of the liquid. Two sets were made in this way. They were
of German-silver wire similar to that used in the "hoop" coils. The
resistance of the first set was 4.503 and 4.509 ohms, and of the second
set 1.490 and 1.505 ohms.

In the preliminary experiments instead of a differential thermometer
two mercury thermometers, graduated to tenths of a degree Centigrade
and readable to hundredths, were used. These were read as nearly
simultaneously as possible. Owing to their comparatively great bulk,
mercury thermometers are not suitable, and so were replaced as soon as
possible by a differential thermometer consisting of four copper-con-
stantan thermo-elements in series. No. 24 constantan and No. 26
copper wire were used. The resistance of the set was about 4.5 ohms.
These were connected to a sensitive Siemens and Halske D'Arsonval
galvanometer of 91.6 ohms resistance, the deflections being observed by
means of a powerful reading telescope to which a glass scale was attached,
the distance from mirror to scale being 150 cm. A deflection of 9.2 cm.
corresponded to a temperature difference of 0°.1 C. The scale could
be easily read to 0.01 cm. The sensitiveness of the apparatus varied to
a certain extent because of the quantity of liquid not being always the
same, and because the heat capacity of the immersed metal also differed
for the different junctions. An idea of the sensitiveness may be gained

from the fact that in the case of the copper-silver junction (see section on copper-silver) a reversal of the heating effect of a current of 0.036 ampere through a coil of 4.5 ohms resistance produced a change of 0.27 cm. per minute in the rate of deflection of the galvanometer. That is, the addition of 2.59 joules of heat (0.62 calories) to one calorimeter would change the deflection of the galvanometer one centimeter. In the case of copper-platinum the addition of 2.18 joules was sufficient to change the deflection of the galvanometer one centimeter.

The stirring of the liquid was first attempted by means of gas stirrers. Each of these consisted simply of a capillary glass tube, one end of which was placed in the bottom of the calorimeter, the other being connected to a tank containing air under a slight pressure. These were used only with the mercury thermometers. It was found that whenever a bubble of air happened to strike the thermometer the latter tended to give the temperature of the air rather than that of the liquid, in consequence rotary stirrers were substituted in the later experiments. These consisted of semi-circular disks of copper, 0.4 cm. radius, soldered to steel knitting-needles. Each was supported and made adjustable by means of two bearings, one at the top of the calorimeter, the other about 7 cm. above it. The stirrers were driven by a small electric motor.

The openings of the calorimeters were partially closed either by cork stoppers, as in the case of copper-silver, or by pieces of cloth laid over the tops of the calorimeters. It was found that when the calorimeters were not shielded in any way the unequal lighting of the room had an appreciable effect upon the amount of heat required by each calorimeter, and in consequence the whole apparatus was surrounded by a box provided with a heating-coil, by means of which, with the aid of a thermostat, the air could be kept at a constant temperature. As will be seen later, it is not important that there should be no heat lost by the calorimeters, but that this loss should be as nearly as possible the same for both. This and other vitiating effects will be discussed under the head of probable sources of error.

Throughout the experiments kerosene was used as the calorimetric fluid, being chosen on account of its mobility and low specific heat. Equal amounts were measured into the calorimeters by means of a pipette. From 35 to 40 c.c. was used in each calorimeter.

In order to be able to determine the temperature difference of the metallic junctions during an experiment when the temperature of the liquid was the same in both calorimeters, they were connected to the galvanometer by means of a double-throw switch so that they could replace the thermo-elements. By determining their thermo E.M.F. by com-

parison, the temperature difference could be computed. This measurement must necessarily be made *after* the current through the junctions is stopped, and in consequence the deflection obtained is less than it should be owing to communication of heat to the liquid.

The approximate temperatures of the experiments were obtained by inserting a mercury thermometer into one of the calorimeters before and after a run and reading the temperature.

Currents were measured by means of Siemens and Halske milliammeters with suitable shunts. The compensating current was supplied by a single storage cell, while the main current was supplied by storage batteries of 4, 6, or 8 storage cells in series, or two sets of 8 cells in series in parallel, depending upon circumstances. The single cell supplied a perfectly uniform current, but the batteries frequently varied as much as one per cent., and occasionally as much as two or three per cent. These variations will not affect the final result materially since the current was read at regular intervals of one or two minutes each.

A sectional view of the calorimeters is shown in Fig. 4, while all the electrical connections are shown diagrammatically in Fig. 5.
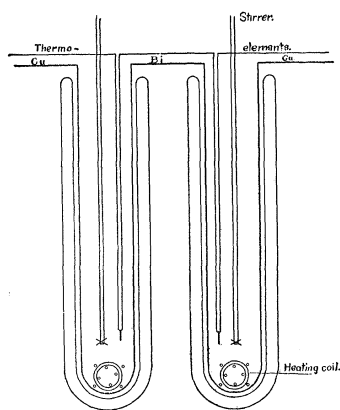

Fig. 4.
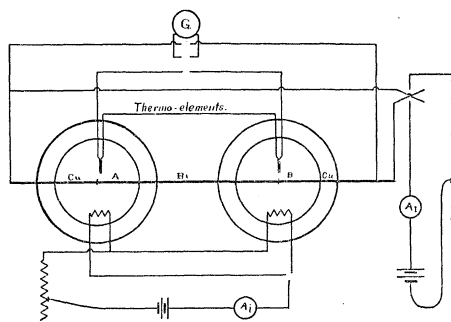
Fig. 5.

Mathematical Discussion.—The following mathematical discussion is somewhat more complete than that given by Barker, to which reference has already been made. If we denote the two calorimeters as *A* and *B*, and for the quantities corresponding to each use the subscripts *a* and *b*, respectively, we may use symbols for the quantities involved as follows:

P = Peltier E.M.F. expressed in volts,

r = resistance of compensating heating-coil in ohms,

R = effective resistance of junction,

i = compensating current in amperes,

I = main current through the junctions,

C = heat capacity of calorimeter and contents *expressed in joules*,

h = rate of heat loss to surrounding bodies dependent upon a differ-
ence in temperature of $1°$ Centigrade,

θ = temperature of liquid minus temperature of surrounding bodies,

s = heat gained from external sources independent of any temperature
differences (*i. e.*, through stirring, etc.).

Case I.—When direction of the current is such that heat is absorbed
in A, and evolved in B, we have

$$\frac{I_a^2 R_a - PI_a + i_a^2 r_a - h_a \theta_a + s_a}{C_a} = \frac{I_a^2 R_b + PI_a - h_b \theta_a + s_b}{C_b},$$

or

$$C_a(I_a^2 R_b + PI_a - h_b \theta_a + s_b) = C_b(I_a^2 R_a - PI_a + i_a^2 r_a - h_a \theta_a + s_a),$$

or

$$PI_a(C_a + C_b) = I_a^2(C_b R_a - C_a R_b) - \theta_a(C_b h_a - C_a h_b) + C_b i_a^2 r_a$$
$$+ (C_b s_a - C_a s_b),$$

whence

$$(1) \quad P = \frac{I_a(C_b R_a - C_a R_b)}{(C_a + C_b)} + \frac{C_b i_a^2 r_a}{I_a(C_a + C_b)} - \frac{\theta_a(C_b h_a - C_a h_b)}{I_a(C_a + C_b)}$$
$$+ \frac{C_b s_a - C_a s_b}{I_a(C_a + C_b)}.$$

Case II.—In a similar way we may obtain the following equation for
the case when the current is reversed.

$$(2) \quad P = \frac{I_b(C_a R_b - C_b R_a)}{C_a + C_b} + \frac{C_a i_b^2 r_b}{I_b(C_a + C_b)} - \frac{\theta_b(C_a h_b - C_b h_a)}{I_b(C_a + C_b)} + \frac{C_a s_b - C_b s_a}{I_b(C_a + C_b)}.$$

Adding equations (1) and (2) we obtain

$$(3) \quad P = \frac{1}{2}\left[\frac{I_a - I_b}{C_a + C_b}(C_b R_a - C_a R_b) + \frac{1}{C_a + C_b}\left(\frac{C_b i_a^2 r_a}{I_a} + \frac{C_a i_b^2 r_b}{I_b}\right) \right.$$
$$\left. - \frac{\frac{\theta_a}{I_a} - \frac{\theta_b}{I_b}}{C_a + C_b}(C_b h_a - C_a h_b) - \frac{\frac{1}{I_a} - \frac{1}{I_b}}{C_a + C_b}(C_b s_a - C_a s_b) \right].$$

If $I_a = I_b$, the first and fourth terms on the right-hand side of the
equation vanish. This condition is easily realized. If, in addition,
$C_a = C_b$, the second becomes $+\dfrac{i_a^2 r_a + i_b^2 r_b}{4I}$, and the third term becomes

$-\dfrac{\theta_a - \theta_b}{4I}(h_a - h_b)$.   Since θ_a and θ_b are both small and approximately equal, the same being supposed to be true of h_a and h_b, the last term may be neglected without any great error.   We have then simply

$$(4) \qquad\qquad P = \dfrac{i_a{}^2 r_a + i_b{}^2 r_b}{4I}.$$

This equation is the one used in all the numerical computations.   It depends as we have seen upon the assumption that $C_a = C_b$.   This condition may not be very fully realized so it is advisable to consider equation (3) a little farther.   Considering only the second and third terms, let us suppose that $C_a + c = C_b$, where c is small in comparison with C_a.   Then

$$P = \dfrac{1}{2I(2C_a + c)}\,[C_a\{i_a{}^2 r_a + i_b{}^2 r_b - (\theta_a - \theta_b)(h_a - h_b)\}$$
$$+\, c\{i_a{}^2 r_a - h_a(\theta_a - \theta_b)\}].$$

If we expand $\dfrac{1}{2C_a + c}$ by the binomial theorem and sum the resultant product as two geometrical progressions we obtain

$$P = \dfrac{1}{4I}[i_a{}^2 r_a + i_b{}^2 r_b - (\theta_a - \theta_b)(h_a - h_b)$$
$$(5)$$
$$+\, \dfrac{c}{2C_a + c}\,\{i_a{}^2 r_a - i_b{}^2 r_b - (\theta_a - \theta_b)(h_a + h_b)\}].$$

Obviously a small difference in the heat capacities of the calorimetric systems will have but little effect upon the final result, unless perchance h_a and h_b should be quite large, which is improbable.

Probable Advantages of Method.—Practically all the methods hitherto employed in the measurement of the Peltier E.M.F. involve temperature differences between the junctions which must necessarily involve both the Thomson and Seebeck effects.   It is impossible to say with certainty what effect these phenomena will have upon the resulting value obtained for the Peltier E.M.F.   These disturbing effects are effectually eliminated by the present method.   This is shown by the temperature differences found for the junctions.   Errors due to loss of heat to surrounding bodies, etc., are reduced to a minimum since the other methods used do not take account of it, and it must have been quite large in some cases.   In other cases it is doubtful whether the temperature differences, or other quantities, measured to determine the amount of heat involved, really were the temperature differences required.   This would be due to a non-

uniform distribution of heat. This matter has been investigated in connection with this work, and has been found to play an important part in the determination of the Peltier E.M.F. This question is discussed at some length in the next paragraph. Another probable advantage of this method is that the Joule heating-effect can be made much smaller than has been the case in some of the previous work. In this way the total range of temperature during a single determination is reduced.

Probable Sources of Error.—As will be observed by referring to the data given for the various couples, the compensating currents were frequently quite different. Several causes may be assigned for this, *e. g.*: (1) difference in rate of heat loss to surrounding bodies for the two calorimeters; (2) difference in the resistance of the immersed portions of the metals forming the junctions, due chiefly to the contact itself, and (3) difference in the heat s. This last is due principally to the stirrers either through heat produced by friction in the bearings or unequal stirring. Only the first of these can have any effect upon the final result [see discussion of equation (3)], unless s should vary during the course of the experiment. This may have happened occasionally, but would probably be as apt to influence the final result in one direction as in the other. Once or twice the speed of the stirrers changed owing to bad contact of the brushes with the armature of the motor. This would affect s. But another and more important effect due to such irregular action of the stirrers is that if the speed of the stirrers is varied in any way the steady temperature condition is upset, causing irregular movements of the galvanometer until a new temperature equilibrium is established. This difficulty actually arose and in consequence several runs gave unreliable results.

Inadequate stirring is a very probable source of error. In such cases the heat added to the liquid will not be distributed uniformly throughout the mass, but will remain in the neighborhood of the places where it is produced. In order to test this point a determination of the Peltier E.M.F. for the copper-bismuth couple was made without stirring the liquid. The result so obtained was 0.0084 volt, or a little more than half the true value. This, too, was the cause of considerable annoyance in the case of copper-platinum. Apparently the platinum foil which was used hung too close to the walls of the calorimeters, thus forming a sort of pocket where, owing to the resistance of the platinum, the liquid became hotter than the rest of the liquid in the vessel. Special precautions had to be observed in order to obviate this difficulty before any consistent set of measurements could be made.

To what extent the difference in rate of heat loss of the calorimeters may have affected the results it is difficult to say. One of the original calorimeters was discarded after it had apparently developed a fracture thus becoming a poor insulator. Afterward when some doubt arose as to the equality of this quantity for the two calorimeters which were used in all the later experiments, a test was made as follows: Both the calorimeters with contents were heated to a temperature of 65° C. and left standing uncovered in an atmosphere at 19° C. In 55 minutes the temperature of the calorimeter A had fallen to 30°.4 C., that of B to 29°.6 C. Several hours afterward both had come to the temperature of the surroundings. This shows that their rates of heat loss were practically equal, but these seem excessively large. The very rapid fall in temperature at first was probably due in part to the rapid evaporation of the kerosene at such temperatures. Another reason might be that a considerable proportion of the surface of the liquid was exposed to the air. Granting that even when the calorimeters are at approximately the temperature of the surroundings the quantity h is still rather large, it does not appear from equation (5) that any error in excess of the ordinary experimental errors should arise from disregarding the terms involving h.

SECOND, OR SHUNT-CURRENT, METHOD.

This method differs from the previous method in that compensation is accomplished by sending more current through one of the junctions than through the other, the difference in the Joule heating-effect being equal and opposite to that arising out of the Peltier effect.

Mathematical Discussion.—The mathematical computation of the Peltier E.M.F. in this case is quite similar to that for the preceding case. Using the same notation as before with the proviso that when $I_a = $ current through junction A, and $i_a = $ shunted current, then $I_a - i_a = $ current through junction B, we have

$$\frac{I_a^2 R_a - I_a P - h_a \theta_a + s_a}{C_a} = \frac{(I_a - i_a)^2 R_b + (I_a - i_a)P - h_b \theta_a + s_b}{C_b}.$$

Clearing of fractions and transposing we have

(1a)
$$\{(C_a + C_b)I_a - C_a i_a\}P = C_b I_a^2 R_a - C_a(I_a - i_a)^2 R_b$$
$$- \theta_a(C_b h_a - C_a h_b) + (C_b s_a - C_a s_b).$$

Similarly with current reversed

(2a)
$$\{(C_a + C_b)I_b - C_b i_b\}P = C_a I_b^2 R_b - C_b(I_b - i_b)^2 R_a$$
$$- \theta_b(C_a h_b - C_b h_a) + (C_a s_b - C_b s_a).$$

Adding, we obtain

$$(3a) \quad \{(C_a + C_b)(I_a + I_b) - (C_a i_a + C_b i_b)\}P = C_b R_a\{I_a{}^2 - (I_b - i_b)^2\} \\ + C_a R_b\{I_b{}^2 - (I_a - i_a)^2\} - (\theta_a - \theta_b)(C_b h_a - C_a h_b).$$

But, if $I_a = I_b$, this reduces to

$$P = \frac{C_b R_a(2I - i_b)i_b + C_a R_b(2I - i_a)i_a - (\theta_a - \theta_b)(C_b h_a - C_a h_b)}{C_a(2I - i_a) + C_b(2I - i_b)}.$$

Let us further assume that (1) $2I - i_a = 2I - i_b$, and (2) $C_a + c = C_b$. Then

$$P = \frac{C_a(R_a i_b + R_b i_a) + c R_b i_a}{2C_a + c} - \frac{(\theta_a - \theta_b)\{C_a(h_a - h_b) + c h_a\}}{(2C_a + c)(2I - i)}$$

$$= \frac{1}{2\left(1 + \dfrac{c}{2C_a}\right)}\left[R_a i_b + R_b i_a + \frac{c}{C_a}R_a i_b - \frac{(\theta_a - \theta_b)\left(h_a - h_b + \dfrac{c}{C_a}h_a\right)}{2I - i}\right].$$

By applying the binomial theorem and grouping terms as was done for the first method we obtain

$$(5a) \quad P = \frac{1}{2}\left[R_a i_b + R_b i_a - \frac{(\theta_a - \theta_b)(h_a - h_b)}{2I - i} \right. \\ \left. + \frac{c}{2C_a + c}\left\{R_a i_b - R_b i_a - \frac{(\theta_a - \theta_b)(h_a + h_b)}{2I - i}\right\}\right].$$

Notice the resemblance this equation bears to equation (5).

As a sufficiently close approximation for numerical work we may use the simplified equation

$$(4a) \quad\quad\quad\quad\quad P = \frac{R_a i_b + R_b i_a}{2}.$$

The assumptions upon which this equation depends are: (1) $I_a = I_b$, (2) $2I - i_a = 2I - i_b$, and (3) disregard of the corrective terms. The first condition is easily realized. The third is the same as that used in deriving equation (4) and nothing further need be said regarding it. In order that the second condition may be assumed without appreciable error it is necessary that I shall be large in comparison with i. Since $P = Ri$, approximately, in order to fulfill this condition the resistance of the junction, R, must be considerable. This is also necessary for a quite different reason. If R were small it would be very difficult to ascertain its value, owing to the effect of the wires leading the current into and out of the bath.

Apparatus.—On this account, for the single determination of copper-nickel each junction consisted of two concentric spirals, one of copper and one of nickel wire. These were wound upon a light fiber frame which just fitted the bottom of the receptacle of the Dewar flask and extended up the sides for a distance of three centimeters. The actual junction was made near the bottom of the vessel. The resistance of each of these junctions was 0.4835 ohm, the wire used being No. 26 copper and No. 23 nickel. The nickel wires in the two junctions were connected by six strands of similar nickel wire twisted together. Heavy copper leads were soldered to the ends of the copper wires. These coils were completely immersed in the liquid. Otherwise the calorimetric arrangements,
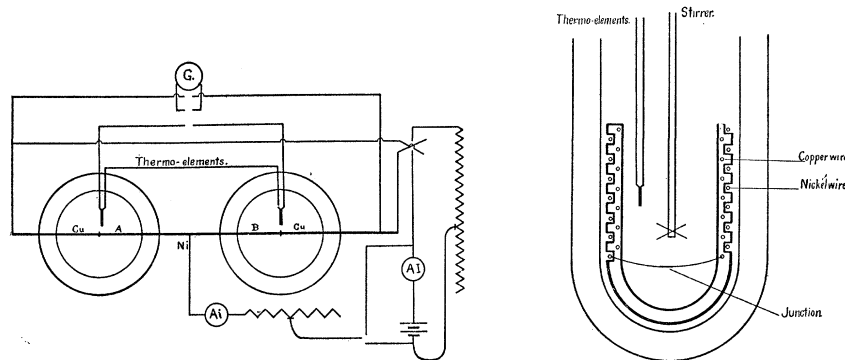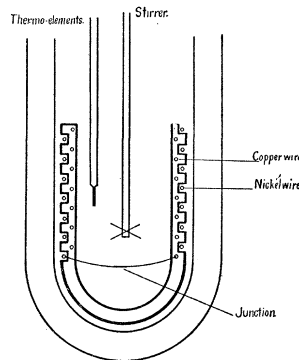

Fig. 6.   Fig. 7.

i. e., stirrers, thermo-elements, etc., were identical with those used for the previous method. For convenience in reading instead of using an ammeter to measure the shunt current it was measured by putting a milli-voltmeter across a standard resistance box through which the current was flowing. The resistance of the voltmeter was 340 ohms. By reading the voltmeter and knowing the box resistance the current could be computed. In most cases a potentiometer would probably be more suitable. By means of a three-way plug-key compensation could be effected in either calorimeter. The electrical connections are shown in Fig. 6, while Fig. 7 represents a cross-section of the bottom of a calorimeter with coil, thermo-elements and stirrer in place.

Probable Advantages.—An advantage which this method apparently possesses over the other is that the heat required to compensate the Peltier heat is produced in the wires which form the junction where the heat is being absorbed. Owing to the greater heat conductivity of the wires, neutralization of the Peltier effect should be accomplished much more readily than when it must all take place through the liquid. The

calorimetric conditions in the two calorimeters are as nearly as possible the same.

Probable Disadvantages.—The total temperature range during an experiment is greater for this method than for the preceding. This is obvious from the fact that the resistance of the junction is very much greater. This might give rise to a greater error since the heat loss is dependent, to a certain extent at least, upon the temperature range. The difficulties attendant upon the stirring are augmented. Otherwise the advantages and disadvantages of this method are substantially those of the preceding method.

Experimental Results.

Copper-Bismuth.

The copper-bismuth junctions were made of two strips of rolled copper plate 2.0×0.24 cm. cross-section, and a strip of bismuth cast for the purpose in the shape of an inverted U. The cross-section of the bismuth was 2.0×0.18 cm. This pair of junctions was the one used for all the preliminary tests of the method. Even the most crude measurements

Table II.

Copper-Bismuth.

I	i_a	i_b	$\dfrac{i_a{}^2 r_a}{4I}$	$\dfrac{i_b{}^2 r_b}{4I}$	P Expressed in Millivolts.
1.037	.1052	.1003	.00816	.00745	+15.61
1.038	.1081	.1015	860	762	16.22
1.957	.1459	.1388	831	756	15.87
.998	.1082	.1014	896	791	16.87
Mean—'hoop' coils 16.14					
1.194	.0969	.0845	.00885	.00674	15.59
1.292	.1183	.0661	1219	382	16.01
1.243	.1172	.0664	1247	400	16.47
.502	.0695	.0505	1082	572	16.54
Mean—final coils 16.13					

which were made did not differ by more than twenty per cent. from the value which was finally found for this couple. When the "hoop" coils were being used over two hours were sometimes required to determine with a fair degree of accuracy the amount of heat required to compensate the Peltier E.M.F. when the current was only sent in one direction. With the form of the coils finally adopted a complete determination could be made in one and a half or two hours. Four trustworthy determinations were made with the "hoop" coils ($r_a = 3.057$, $r_b = 3.072$),

and after these were replaced by coils of the final type ($r_a = 4.503$, $r_b = 4.509$) four other determinations were made. The data and results for these eight determinations are given below and separately averaged. All the values are for an approximate mean temperature of 18° C. Heat was absorbed when the current passed from bismuth to copper, and was given out when the direction of the current was from copper to bismuth. That is, using the same convention as Jahn and others, the sign of the Peltier E.M.F. is positive.

The Peltier E.M.F. between copper and bismuth is, therefore, $+0.01613$ volt at 18° C.

The extreme variation of these eight determinations is 8 per cent.; hence, the probable error is less than one per cent.

Copper-Silver.

The copper-silver couple was made of rolled copper strips, 1.0×0.25 cm. in cross-section, and a silver strip, 0.9×0.2 cm. in cross-section, rolled from a block of pure silver. Several trial runs were made, but because the magnitude of the Peltier effect was so small no satisfactory results were obtained. The values ranged from zero to $+ 0.00006$ volt. These values are of the same order of magnitude as the experimental errors. The method finally adopted was to determine the rate of change of the deflection of the galvanometer while a compensating current of measurable magnitude was being supplied first to one heating-coil and then to the other. During this time no current was sent through the junctions. Then while no compensating current was being supplied, a current was sent through the junctions in one direction and the deflection at the end of every minute for an interval of from 20 to 30 minutes plotted. From this plot an average rate of change of deflection was obtained. The same was done with the current flowing in the opposite direction. Two such runs were made, the same current being sent through the junctions in each case.

When a current of 0.036 ampere was first sent through the heating-coil in calorimeter A and then changed to calorimeter B the change in the rate of change of deflection was 0.27 cm. per minute, the resistances of the coils being 4.503 and 4.509 ohms, respectively. From this it follows, as was pointed out in connection with the sensitiveness of the apparatus,

that $\dfrac{0.036^2 \times 4.5 \times 60 \times 2}{0.27} = 2.59$ joules of heat added to one calorimeter will change the deflection of the galvanometer one centimeter.

The results for rate of change of deflection with the current flowing through the junctions were as follows:

TABLE III.

Copper-Silver.

	I	Direction of Current in A.	Rate of Change of Defl. per Min.
First run	4.65	Cu to Bi	+.02 cm.
Second run	4.65	Cu to Bi	+.028
First run	4.65	Bi to Cu	+.01
Second run	4.65	Bi to Cu	+.01

First run — diff. in rate of change of defl. per min. = .01 cm.

Second run — diff. in rate of change of defl. per min. = .018 cm.

Positive deflection indicates that the temperature of A is greater than that of B.

$$P \text{ (First run)} = + \frac{0.010}{0.27} \left(\frac{2 \times 0.036 \times 4.5}{4 \times 4.65} \right) = + 0.000023 \text{ volt.}$$

$$P \text{ (Second run)} = + \frac{0.018 \times 0.000023}{0.010} = + 0.000041 \text{ volt.}$$

The mean temperature of these two runs was approximately 18° C.

The Peltier E.M.F. between copper and silver is, therefore, +0.00003 volt at 18° C. The probable error is less than 0.00001 volt.

Notice that this result is very slightly positive, agreeing with that of Edlund, but is quite different from the value obtained by Jahn (see Table X. below).

A single determination at a temperature of 48° C. gave $P = 0$.

Copper-Aluminium.

The copper strips used were the same ones used in the case of copper-silver. Aluminium wire 0.5 cm. in diameter was used. The ends were flattened so that the immersed portions were 1 cm. wide, thus making their cross-section about the same as that of the silver. Only five runs were made. The first was merely a trial run and is omitted from the following table. The same heating-coils were used as in the previous experiment.

TABLE IV.

Copper-Aluminium.

I	i_a	i_b	$\frac{i_a^2 r_a}{4I} \times 10^3$	$\frac{i_b^2 r_b}{4I} \times 10^3$	P in Millivolts.	Approximate Mean Temp.
4.86	.0436	.0320	.4424	.2375	+.680	13.6° C.
5.12	.0463	.0337	.4713	.2501	.721	16.3
4.00	.0405	.0297	.4614	.2485	.710	18.1
5.60	.0461	.0347	.4271	.2423	.669	15.2
				Means........	.695	15.8

The extreme range of these values is 7.4 per cent. of the mean. The probable error involved is about one per cent. We may, therefore, conclude that for copper-aluminium $P = +0.00070$ at 16° C.

Copper-Platinum.

The same copper strips were used as in the two preceding cases. The most suitable piece of platinum available was a piece of foil about 2 cm. wide and 33 cm. long. Its cross-section was approximately 0.0104 cm.² Considerable difficulty was experienced in getting anything like consistent results with this couple. The difficulty no doubt arose from insufficient stirring of the liquid. Apparently the foil rested against the glass wall of the calorimeter in such a way as to separate a part of the liquid from the main body. This would be heated to a different temperature, and the amount of heat conducted to or from it by the remaining liquid would be dependent upon this difference in temperature. It was only after the greatest precautions had been taken to prevent the reoccurrence of this pocketing effect (such as folding in the corners of the foil and inserting small pieces of cork between it and the glass) that consistent results were obtained. Five determinations were made with the apparatus as finally adjusted. The fifth was a repetition of the second, which gave a result for P of $+ 0.00121$ volt. These two determinations were made with a larger current than was used in the other three cases, and so the difficulty previously mentioned evidently reappeared in the second determination, which has been omitted on that account from the following table of results. In repeating this determination greater care was taken to insure good circulation of the liquid. Heating-coils of 1.49 and 1.505 ohms resistance were used so as to have larger compensating currents.

A current of 0.1097 ampere through the smaller resistance produced a change in the rate of deflection of the galvanometer of 0.494 cm. per minute. From this it follows that 2.18 joules of heat added to one calorimeter would change the deflection of the galvanometer one centimeter.

Table V.

Copper-Platinum.

I	i_a	i_b	$\dfrac{i_a^2 r_a}{4I} \times 10^3$	$\dfrac{i_b^2 r_b}{4I} \times 10^3$	P in Millivolts.	Approximate Mean Temp.
1.902	.0522	.0326	0.537	0.210	+0.747	17.0° C.
1.533	.0437	.0412	.464	.416	.880	16.3
1.035	.0445	.0195	.713	.138	.851	18.1
2.85	.0546	.0623	.390	.512	.902	17.2
				Means........	.845	17.1

The extreme range of these values is 5.5 per cent. of the mean, hence, the probable error is about one per cent.   For copper-platinum $P = + 0.00085$ volt at $17°$ C.

Copper-Nickel.

The apparatus used in this experiment has been described already in connection with the second method.   The first two determinations given below were made on the day previous to the last two, and are considerably higher than the latter.   The values corresponding to the higher temperatures are higher than the others, also one compensating current shows a marked tendency to increase with the temperature, the other to decrease.   This indicates that the rate of heat loss to the surroundings was not the same for the two calorimeters.   On the whole it seems that this method is not as satisfactory as the first method.   This is doubtless due to the preponderance of the Joule heat.

TABLE VI.

Copper-Nickel.

I	i_a	i_b	P	Approximate Mean Temp.
0.650	.01463	.00950	+ .00583	19.2° C.
.701	. 1410	1520	708	25.0
.571	1206	1015	537	19.6
.611	1091	1329	585	24.0
		Means........	603	22.0

The extreme variation of these values is 28.4 per cent. of the mean. Even assuming that the Peltier E.M.F. increases quite rapidly with the temperature the probable error must still be quite large.   We shall take $+ 0.0060$ volt to be the value of the Peltier E.M.F. between copper and nickel at $22°$ C.

SUMMARY OF RESULTS.

The values obtained for the Peltier E.M.F. for the couples investigated are tabulated below.

TABLE VII.

Metal Against Copper.	Peltier E.M.F. Expressed in Millivolts.	Temperature.
—		
Copper......................	——	——
Silver.......................	0.03	18° C.
Aluminium...................	0.70	16
Platinum.....................	0.85	17
Nickel.......................	6.0	22
Bismuth.....................	16.1	18
+		

JUNCTION DEFLECTIONS.

From the junction deflections it appeared that in the case of copper-bismuth the difference in temperature of the junctions at the end of a run varied from $0°.05$ C. to $0°.1$ C. For copper-silver and copper-aluminium the junctions appeared to have the temperature of the liquid. In the case of copper-platinum the results were variable, but certainly never greater than $0°.1$ C. The maximum difference observed for copper-nickel was $0°.16$ C.

THERMO E.M.F. AND THE PELTIER E.M.F.

In order to test the validity of Thomson's theorem, which has been mentioned already, viz., $P = T \dfrac{dE}{dT}$ where E is the thermo E.M.F. at the temperature T, the thermo E.M.F. of the various couples was determined. One junction was kept at a temperature of $0°$ C. by being

TABLE VIII.

Thermo E.M.F.

Metal Against Copper.	Resist.	Defl. in Cm.	Temp. Diff.	Thermo E.M.F. in Microvolts.	P Computed in Millivolts.
Bismuth........	10,280	27.59	32.70	+55.07	
Bismuth........	7,780	35.84	32.22	54.96	
Bismuth........	7,280	37.43	31.75	54.49	
Mean (Abs. Temp. = 291).......				54.84	+15.96
Silver..........	420	4.76	34.66	+ 0.366	
Silver..........	420	3.92	34.40	.306	
Silver..........	680	.58	32.08	.078	
Silver..........	480	.59	31.02	.058	
Mean (Abs. Temp. = 291)				.202	+ 0.06
Aluminium	680	21.80	29.52	+ 3.07	
Aluminium	420	39.15	31.58	3.11	
Mean (Abs. Temp. = 289).......				3.09	+ 0.89
Platinum.......	3,280	4.72	39.50	+ 2.41	
Platinum.......	1,280	11.19	38.52	2.29	
Platinum.......	2,280	6.00	37.70	2.23	
Platinum.......	3,280	4.01	37.10	2.18	
Platinum.......	1,680	8.20	35.90	2.36	
Mean (Abs. Temp. = 290)				2.29	+ 0.66
Nickel....	10,280	16.92	49.50	+21.61	
Nickel.........	12,280	13.82	48.54	21.50	
Nickel.........	8,280	19.92	47.22	21.48	
Nickel.........	10,280	15.31	45.14	21.44	
Mean (Abs. Temp. = 295)				21.51	+ 6.35

immersed in a bath of melting ice; the other junction was immersed in a water bath approximately as much above the temperature at which the Peltier E.M.F. was measured as 0° C. was below it. The E.M.F. was measured by connecting the thermo-element in series with a sensitive galvanometer and a standard resistance box. When used with the first three couples its deflection constant was 6.35×10^{-9} amperes per centimeter; with the last two the constant was 6.15×10^{-9}. Its resistance was 280 ohms. The galvanometer was badly damped when only a small resistance was in circuit with it and so the measurements with the copper-silver couple are not very reliable. The second pair of readings given for that couple were taken three hours after the first. The difference is probably due to a change in the temperature of some of the connections. In any event it is certain that the sign of the thermo E.M.F. of this couple was positive. Table VIII. gives the data obtained together with the computed values of the Peltier E.M.F.

COMPARISON OF RESULTS OBTAINED BY DIFFERENT INVESTIGATORS.

In the following table the results of Le Roux, Jahn, Edlund (as computed in the first part of this paper), a few scattered results, and the results of the present investigation are grouped together. The calcu-

TABLE IX.

Results Obtained by Different Investigators, Expressed in Millivolts.

Metal Against Copper.	LeRoux.		Jahn.		Edlund.		Caswell.		Observed by Others.
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
Antimony .	− 5.64	.300							
Iron	2.93	.224	−3.68	−3.07	− 2.96	− 3.08			−3.06[1]
Cadmium .	.53	.232	.72	.72	.16	.21			
Zinc	− .45	.614	.68	.41	− .01	− .02			
Copper . . .	——	——	——	——	——	——	——	——	——
Silver			− .48	− .58	+ .03	+ .04	+ .03	+ .06	
Gold					.33	.50			
Lead					.50	.57			
Tin					.56	.82			
Aluminium					.70	.89	.70	.89	
Platinum .			+ .37	+ .38	1.02	1.23	.85	.66	
Palladium .					2.17	2.43			
Nickel			+5.07	+5.44			6.0	6.35	{ +6.75[2] +8.04[3]
Bismuth . .	+22.3	.263			+17.7	+17.6	+16.1	+16.0	

[1] Lecher's derived value of the Peltier E.M.F. between iron and *silver*.

[2] Barker.

[3] Cermak.

lated values have been obtained by means of Thomson's equation. The second column of values given for Le Roux contains the ratios of his values of the Peltier E.M.F. to thermo E.M.F. in relative units.

For all of these values I have aimed to retain only as many significant figures as seem to be justified by the accuracy of the experiments.

PHYSICS LABORATORY,
STANFORD UNIVERSITY,
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