



# LV. The thermo-electric properties of some liquid metals

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LV. *The Thermo-electric Properties of some Liquid Metals.*  
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THE object of the experiments here to be described was to compare the thermo-electric properties of solid metals with those of the same metals when melted. The four metals employed, tin, lead, bismuth, and mercury, were each thermo-electrically compared with copper, the tested metal being contained in a hard glass tube, so that the observations could be pushed to temperatures considerably above those of the melting metals, and the changes in the thermo-electric properties during the process of melting observed. Two sets of experiments were made, the first set with the greater part of the metal under test at ordinary temperatures, and the second set with all the metal under test at high temperatures.

In the first set of experiments with tin, lead, and bismuth, the glass tube containing the metal was W-shaped, the metal filling the central part, but only rising about one-third of the height in the outside limbs. To fill this tube one end was dipped into a crucible full of the melted metal, which was then allowed to cool. The crucible and tube were immersed in a bath of linseed oil, which was raised to a temperature above that required to melt the metal. When the metal was quite liquid, air was withdrawn from the upper end of the tube till the metal had risen to the right height. The tube was next slowly withdrawn from the still hot oil, to prevent

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cracking due to the freezing of the metal, and allowed to cool. The superfluous metal was then melted out of the open limbs. The two copper-metal junctions were to be in the two open limbs of the tube, and a number of thick copper wires were so arranged round the outside of the tube as to conduct away the heat from all parts not in the immediate neighbourhood of the hot junction. By this means all the metal except a small portion was kept solid, and the level of the melted metal was always higher in the open than in the closed limb. This was necessary, as the solid metal was not a satisfactory cork for the tube, and a slight liquid pressure was needed to keep good contact between the liquid and solid metal.

The temperature-differences between the hot and cold junctions were measured with a thermo-element of platinum and a platinum-rhodium alloy (Pt 90 per cent., Rd 10 per cent.). This thermo-element was calibrated between the temperatures of 0° C. and 263°·5 C. by comparison, in linseed oil, with a Reichsanstalt standardized thermometer. The calibration curve was then extrapolated as far as 430° C. by means of an equation. For reasons which will be explained later, it was useless to adopt any more accurate method than this for the first set of experiments. The thermo-element was insulated within and from without with asbestos paper, and each junction was bound to one of the standard copper wires. These copper wires were also insulated with asbestos, so that only their ends, which were in close proximity to the junction of the temperature-measuring thermo-element, were uncovered.

Some experiments were made to determine the electrical insulating properties of asbestos paper at high temperatures, and it was found that the errors introduced by the electrical conductivity of the supposed insulator were, up to 600° C., negligibly small. Other experiments were made to determine whether or not the temperature of the junction in asbestos differed greatly from the temperature of the metal surrounding the asbestos. One junction of the temperature-determining thermo-element was immersed in melted lead, and the other in melting ice. The parts of the wires just outside the lead were alternately heated with a burner, whereby the temperature-difference between the junction and the metal would be decreased, and cooled with an air blast, whereby the temperature-difference would be increased. Readings of the temperature-difference between the two junctions were meanwhile taken; and it was found that by varying the temperature of the leading-in wires the tempera-

ture of the hot junction was not altered by more than  $\frac{1}{10}$  of a degree. As the leading-in wires were hotter, when warmed by the flame, than the melted lead,  $\frac{1}{10}$  degree was greater than the greatest error introduced during the experiments by the heat-insulating capability of the asbestos paper.

Each of the copper wires with its thermo-element junction was melted into the metal in its respective limb, and held in the centre of the tube by asbestos paper. One limb of the W was heated in a sand bath, and the other was kept cold in melting ice.

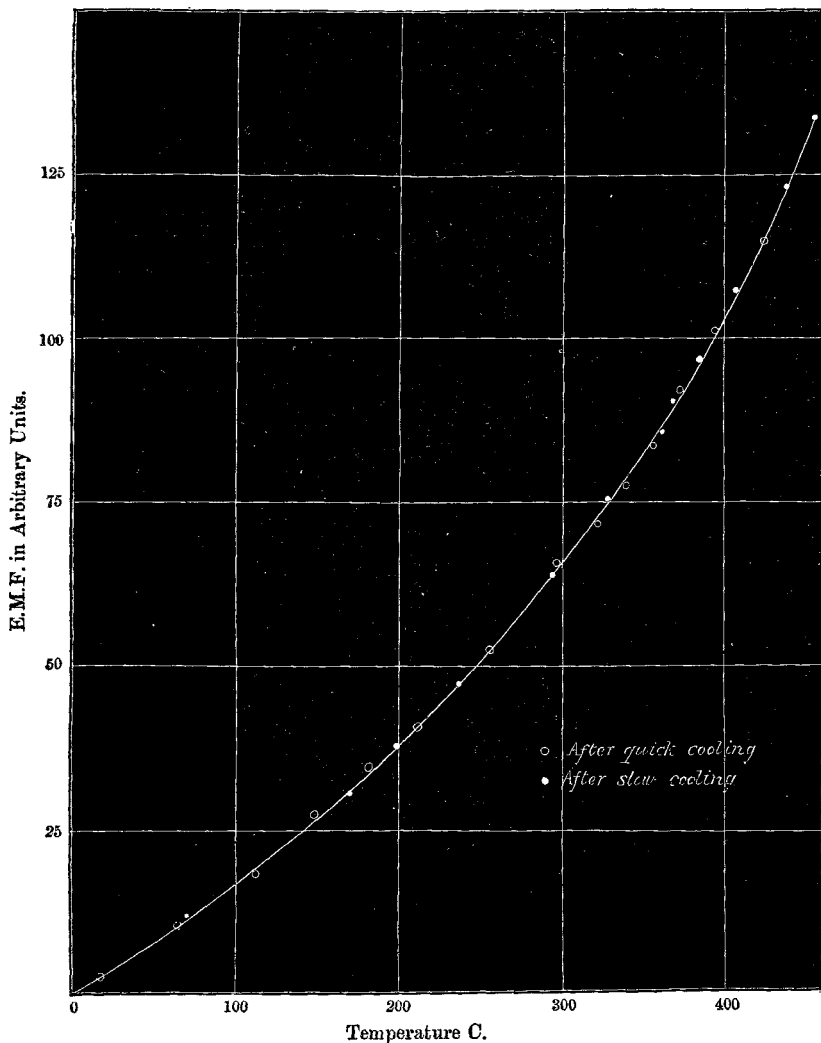
The two standard copper wires and the two free wires from the temperature-determining thermo-element were led to a paraffin switch-block, so that either pair could be connected, through a reversing key and a resistance, to a reflecting galvanometer. This resistance was so great as to render no correction necessary for the resistance variations, due to heat, in the circuit. For each reading the temperature of the hot junction was made nearly constant; then, using each thermoelectric combination alternately, galvanometer deflexions were noted with the current direct, and the current reversed. After the necessary correction, the mean of the readings of the platinum-platinum-rhodium thermo-element gave the temperature, and the mean of the readings of the thermo-element under test gave the E.M.F. in arbitrary units. After each complete experiment, the constant of the temperature-measuring thermo-element was determined by removing the crucible containing sand, putting in its place one containing melted lead, and allowing the lead to cool, meanwhile taking readings.

The curves for copper-lead, copper-tin, and copper-bismuth, which were obtained by this method, are given in figs. 1, 2, and 3 respectively. The abscissæ are temperatures and the ordinates E.M.F.'s in arbitrary units. These curves will be discussed when the mercury experiments have been described.

The W-shaped tube was not suitable for the application of a freezing-mixture, and so in the mercury experiments the junctions were each in a small test-tube about half filled with the metal. An inverted U-tube also full of mercury, with one end dipping into the metal in each of the test-tubes, connected the two. One of the test-tubes was surrounded by melting ice, and the other was cooled with a mixture of solid carbon dioxide and ether. A mass of copper wire was wrapped round the tube to be cooled, in order that it might warm up slowly after the evaporation of the carbon dioxide.

As the temperatures to be measured approached the neutral point of the thermo-element used in the last experiments, an iron-constantan thermo-element was employed to measure

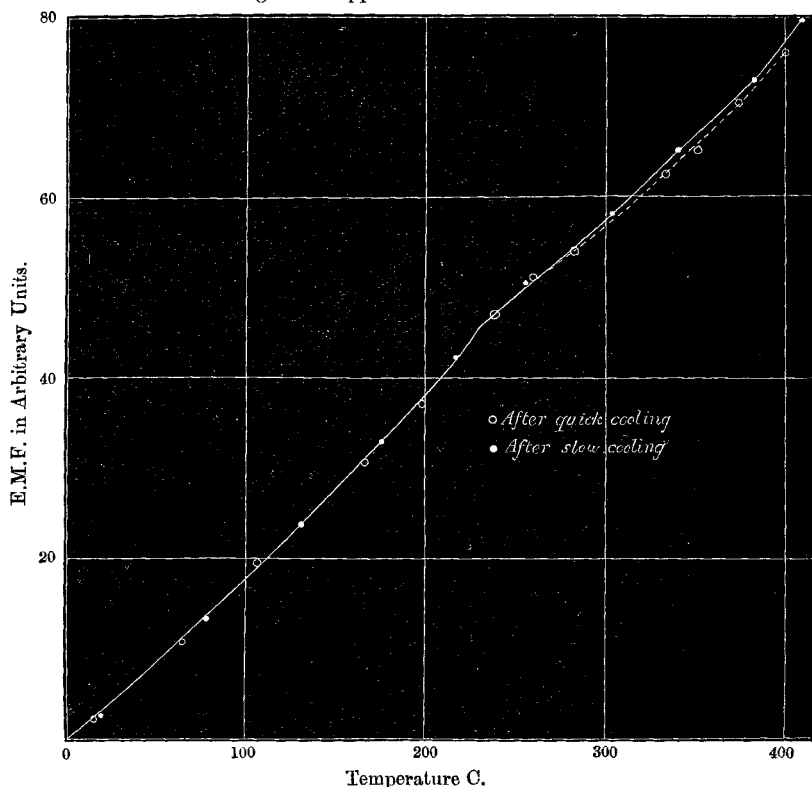
Fig. 1.—Copper-Lead Thermo-element.



the temperature-differences between the two junctions. This thermo-element was calibrated by the observation of the galvanometer deflexions when one junction was in melting ice

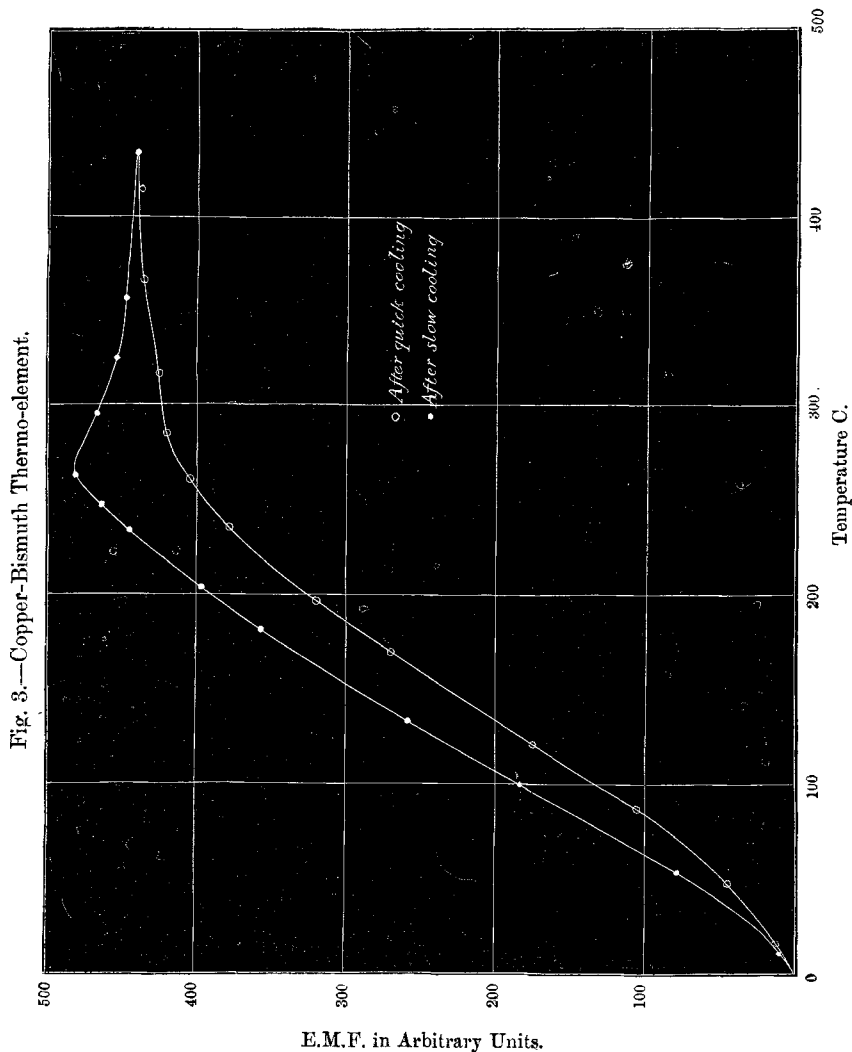
and the other junction first in melting mercury and then in boiling carbon dioxide and ether. As these two deflexions were nearly proportional to their respective temperature-differences, the calibration curve equation was assumed to be of the form, deflexion  $= at + bt^2$ , where  $t$  is the temperature, and  $a$  and  $b$  constants. These two constants were determined from the two observations, and the calibration curve for the thermo-

Fig. 2.—Copper-Tin Thermo-element.



element was plotted from the equation. The element and the standard copper wires were insulated as in the last experiment, and bound to the glass tubes dipping into the mercury. The freezing-mixture was contained in a double-walled test-tube, the inner and outer walls being separated by cork distance-pieces, and the whole being wrapped in flannel. The electrical connexions were the same as in the last experiment.

In the experiments, the tube containing the cold junction was cooled as far as possible with the freezing-mixture, and allowed to warm slowly up. Readings of the galvanometer were meanwhile taken every thirty seconds, as follows:—

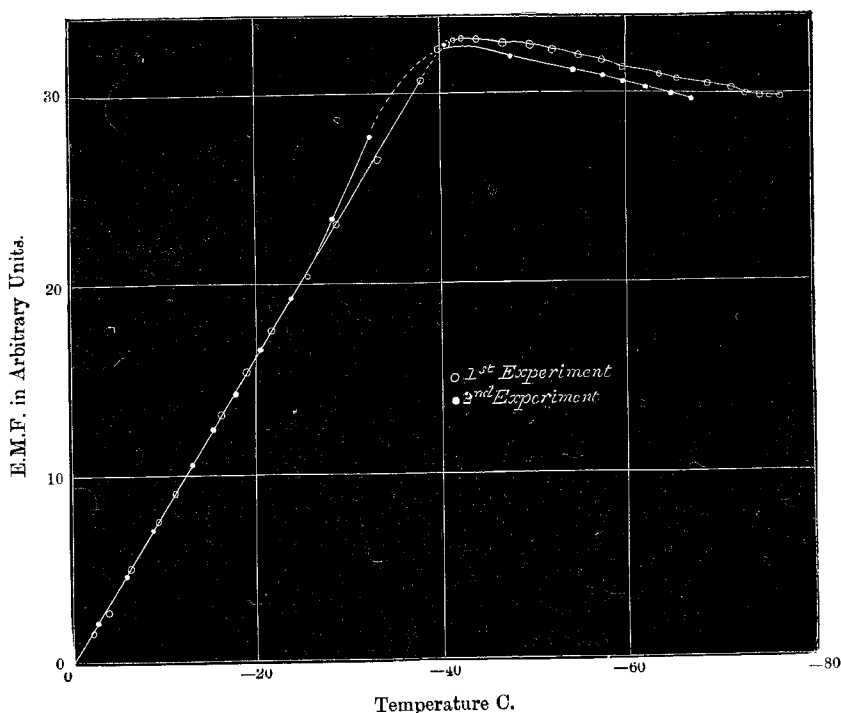


First, a reading from the temperature-determining thermo-element with the current direct; then a reading from the same element with the current reversed; then a reading from

the copper-mercury element with the current direct; and lastly, a reading from this element with the current reversed. The cycle then began again. From the means of each pair of readings, reduced, two curves were plotted, one giving the relation between temperature and time, and the other giving the relation between E.M.F. in arbitrary units, and time.

The curves (fig. 4) give the relation between E.M.F. and temperature deduced from these two curves, for two experiments.

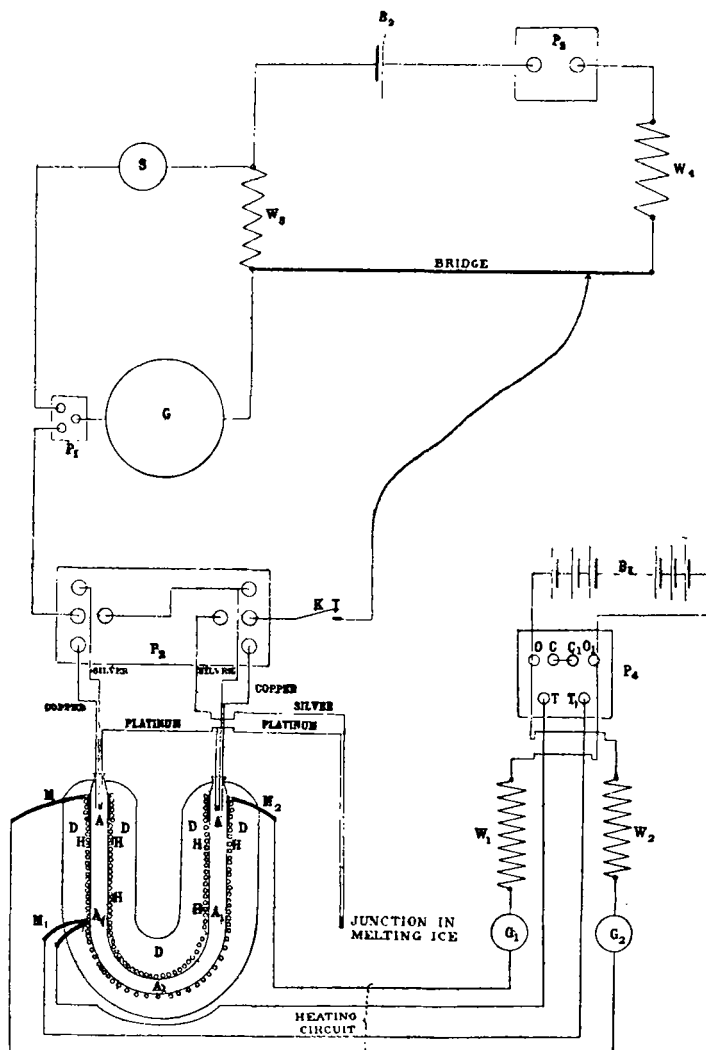
Fig. 4.—Copper-Mercury Thermo-element.



In figs. 2, 3, 4 two curves are in each case given. These two curves were obtained from the same metal. The effect is most marked with bismuth (fig. 3). At the conclusion of one experiment the apparatus was cooled very rapidly by removing the sand and blowing air on to the tube containing the melted metal. Another set of readings was then taken, with the temperature of the hot junction rising, and the lower of the two curves in fig. 3 was obtained. At the conclusion of this experiment the apparatus was cooled very slowly, about two hours being occupied, and the result of the next

experiment was the upper curve. It was found possible, moreover, with intermediate rates of cooling to produce intermediate curves. This effect is probably due to the

Fig. 5.



variations in the crystalline structure of the metal under test, dependent on the rapidity of its solidification; and it may be that the various thermo-electric properties which have been

observed for different pieces of bismuth are largely due to this same cause. With tin the effect was less marked, and with lead it was unnoticeable. In the mercury experiments it was not possible to regulate the rate of cooling; but the two most widely differing curves obtained are given in fig. 4.

As this effect of its previous treatment upon the metal rendered accuracy impossible, the experiments were repeated with three of the metals, viz. tin, lead, and bismuth, with a method so arranged that the whole mass of the metal to be tested was in a molten state, and thus homogeneous.

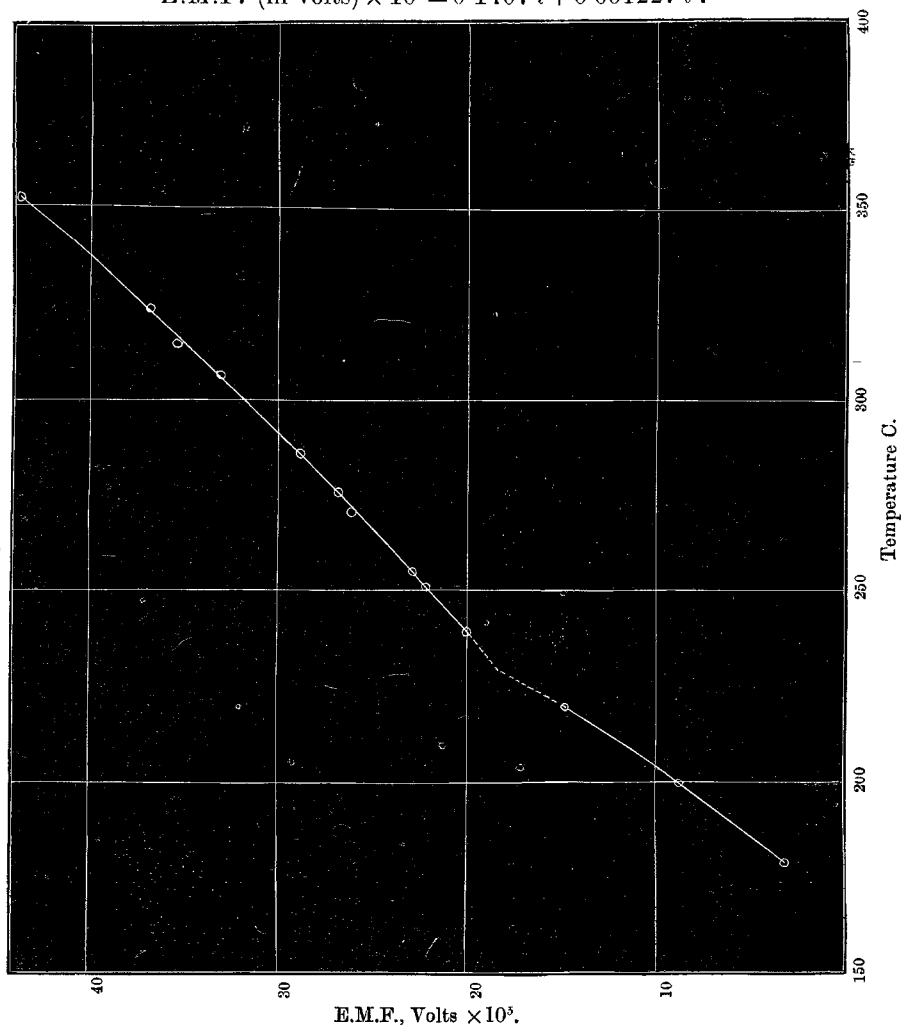
The apparatus is shown in fig. 5. The metal was contained in a U-tube A A<sub>1</sub> A<sub>1</sub> A, and was heated by a current of electricity in german-silver wires H H H. The metal was introduced into the tube by means of a glass pipette, both tube and pipette being warmed in a bunsen flame. The part of the glass tube where the junctions were to be, A A, was covered with copper to render the heat distribution more uniform. The german-silver wire was insulated with asbestos paper, and wound spirally round the tube in two sections, M M<sub>1</sub>, M<sub>1</sub> M<sub>2</sub>. Over this were wrapped several layers of asbestos paper and asbestos string, DD. The connexions of the heating circuit are shown in fig. 5. In the paraffin switch-block, P<sub>4</sub>, if T C and T<sub>1</sub> C<sub>1</sub> were connected, the same current from the heating battery passed through both ammeters, G<sub>1</sub> G<sub>2</sub>, both resistances, W<sub>1</sub> W<sub>2</sub>, and both sections of the heating coil. This caused a saving in current when it was merely required to melt the necessary connexions into the metal, or to burn out the asbestos insulation. If, however, T O was connected the current passed through the ammeter G<sub>1</sub>, the resistance W<sub>1</sub>, and the long section of the heating coil; and if T<sub>1</sub> O<sub>1</sub> was connected the current went through the other ammeter, resistance, and heating-coil section. By adjusting the resistances W<sub>1</sub> and W<sub>2</sub> the temperatures at the junctions could be varied as required. The diameter of the german-silver wire was 0.5 mm., and the largest current required was 4 amperes. The U-tube is shown about one half actual size.

For measuring the temperatures a platinum-silver thermo-element was employed, as this gave E.M.F.'s of the same order of magnitude as those to be measured. This element had three junctions, as shown in fig. 5, so that either the temperature of one of the junctions or the temperature-difference between the two junctions of the thermo-couple under test could be measured. The thermo-element was calibrated with linseed oil up to 288° C.; and one point on the calibration curve, at 441.4° C., was determined with

sulphur vapour. Each limb was calibrated separately, but they were found to be similar. The part of the calibration curve from  $288^{\circ}$  C. to  $430^{\circ}$  C. was plotted from the equation :—

$$\text{E.M.F. (in volts)} \times 10^5 = 0.1407 t + 0.001227 t^2.$$

Fig. 6.—Copper-Tin Thermo-element.

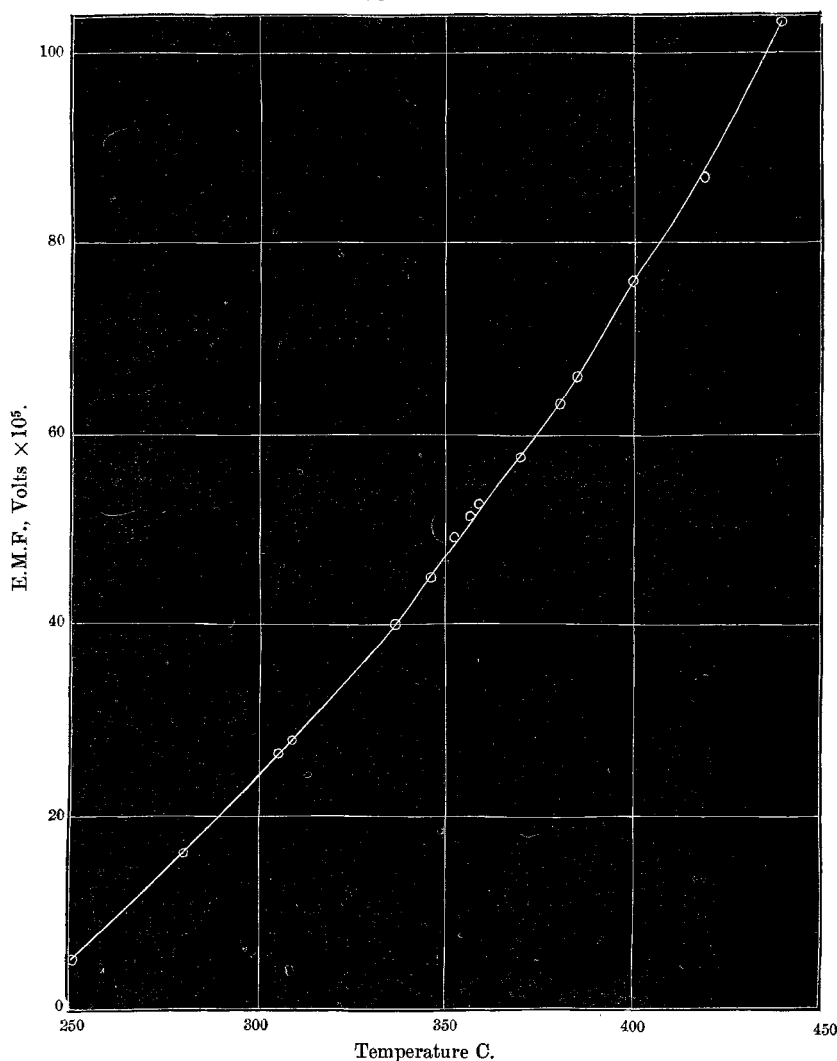


This equation was obtained from the point on the curve determined with sulphur, and the point where  $t=220^{\circ}.7$  C. on the curve as drawn in between  $0^{\circ}$  C. and  $288^{\circ}$  C. By the application of the method of least squares to all the calibra-

tion observations a somewhat different equation was obtained,  
viz. :—

$$\text{E.M.F. (in volts)} \times 10^5 = 0.1463 t + 0.001238 t^2 ;$$

Fig. 7.—Copper-Lead Thermo-element.

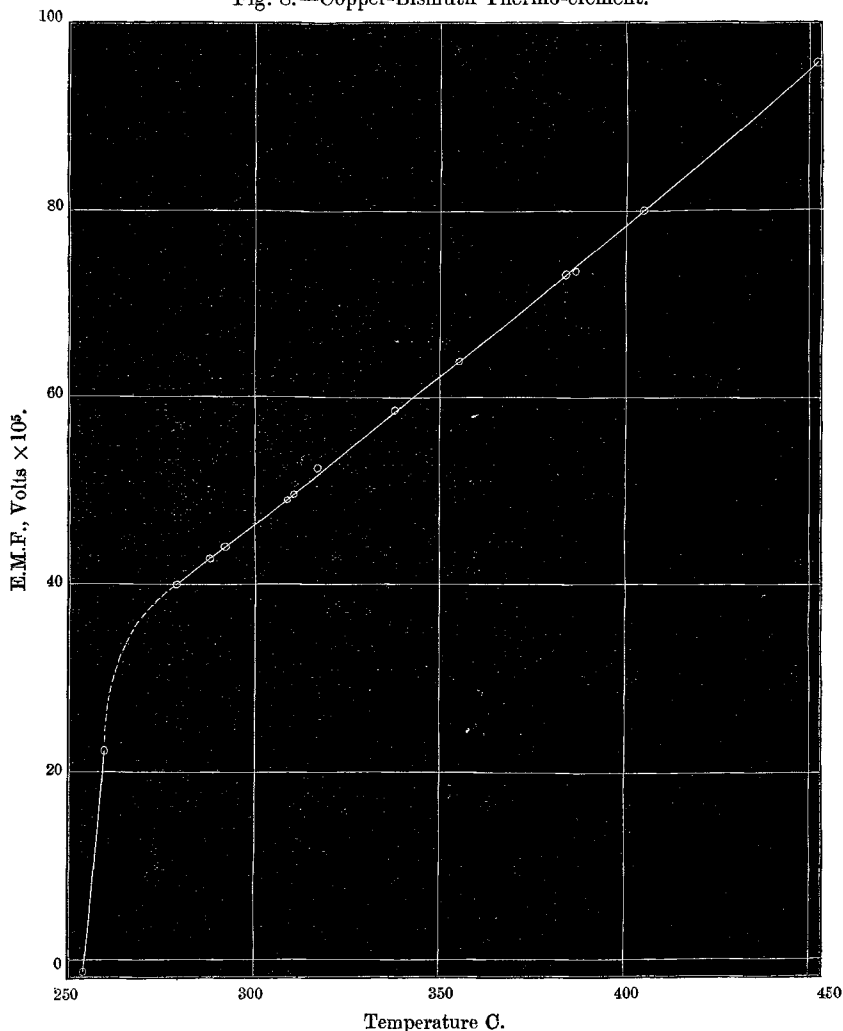


but as the calibration curve was not exactly a parabola the upper equation was judged the better.

The junctions and standard copper wires were insulated as

in previous experiments and melted into the metals. The two standard wires and the three free wires from the temperature-determining thermo-element were led to a paraffin switch-block,  $P_2$ , which was connected to an arrangement of

Fig. 8.—Copper-Bismuth Thermo-element.



a galvanometer,  $G$ , a standard cell,  $S$ , a key,  $K$ , a bridge battery,  $B_2$ , resistances,  $W_4$  and  $W_3$ , switch-blocks,  $P_1$  and  $P_3$ , and a metre bridge, as shown in fig. 5, for measuring the E.M.F.'s.

The current in the long heating section was adjusted before each reading till the temperature of the fixed temperature junction was at a certain point, slightly above the melting-point of the tested metal. Readings were taken with the temperature of the variable temperature junction both above and below the melting temperature of the metal. With tin and lead this latter was easy, but with bismuth, owing to the crystallization effect before mentioned, the readings were rather uncertain. Above the melting-point, however, they were perfectly constant.

The curves plotted from the results of the experiments by this method are given in figs. 6, 7, and 8 respectively.

In each of these curves we see that in a small variation of temperature, about the melting-point, there is a considerable change in the direction of the thermo-electric curve. The effect is smallest with lead, with tin it is larger, and with bismuth it is very remarkable; that metal changing, during melting, from an exceedingly active thermo-electric metal to one very similar to lead in its thermo-electric properties. With mercury also (fig. 4) we see that a great change takes place at the melting-point. This indicates that there is a difference between the Peltier effect for the solid and for the melted metal. But the change in curvature is not sufficiently marked for us to be able to say whether the specific heat of electricity remains proportional to the absolute temperature. To decide this point a direct determination of the Thomson effect is needed.

The worked-out observations from which the curves in figs. 6, 7, and 8 were plotted are given below.

*Copper-Tin Element.* (Fig. 6.)

Temperature of constant temperature junction 239° C.

Temperature of variable temperature junction.	E.M.F. in volts $\times 10^5$ .
255.8	2.86
276	7.01
286.1	9.0
306.1	13.2
323.2	16.92
353.7	23.63
251	2.0
272.2	6.35
315.1	15.45
219.7	-5.1
200.1	-11.15
179.5	-16.86

*Copper-Lead Element.* (Fig. 7.)Temperature of constant temperature junction  $336^{\circ}\cdot 1$  C.

Temperature of variable temperature junction.	E.M.F. in volts $\times 10^3$ .
346.1	5.215
357	11.13
370.6	17.92
385.2	26.5
400.5	35.86
418.3	47.4
440.3	63.2
359.1	12.25
352.8	8.5
380.2	23.75
310.3	-11.9
307.3	-13.4
280.5	-23.6
251	-35

*Copper-Bismuth Element.* (Fig. 8.)Temperature of constant temperature junction  $278^{\circ}\cdot 5$  C.

Temperature of variable temperature junction.	E.M.F. in volts $\times 10^5$ .
287	2.6
291.4	3.97
308	9.01
315.7	12.05
356.7	24.5
385.1	33.68
405.9	40.15
453.6	56.25
388.3	34.18
339.2	18.94
309.2	9.73
259	-18.01
254.6	-41.2

In each case a constant has been added to the E.M.F.'s before plotting.

These experiments were conducted in the Physical Laboratory of the Eidgenössisches Polytechnikum, Zürich, under the supervision of the director, Prof. Dr. H. F. Weber, to whom my best thanks are due.