

THE THERMOELECTRIC PROPERTIES OF
LIQUID ALLOYS OF
MERCURY AND TIN

BY

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Since 1824 when Thomas J. Seeback discovered that if the junction of any two unlike metals was heated an electromotive force was produced, much experimental work has been done in this field. When two such metals are joined the apparatus is called a thermocouple. The laws relating the electromotive force produced and the difference of temperature between the ends of the thermocouple are fairly definitely known in the case of solid metals and solid alloys, which are pure, being used as the arms of the thermocouple. Less is known in the case of pure liquid metals (see *Annals de Physique*, Mai-Juin, 1920), and nothing has been done in the case of an arm of the thermocouple being an alloy in the liquid state.

Therefore, in brief, the objects of this research were:

1. To study the E.M.F.-Temperature relation in a thermocouple in which one arm was pure mercury and the other was an alloy of mercury-tin in the liquid state.

2. To attempt to establish a relation between the thermoelectric properties of mercury-tin alloys and the resistivity of mercury-tin alloys. The latter question had been studied in a research by

G.V. Emery at the University of Kansas in 1924.

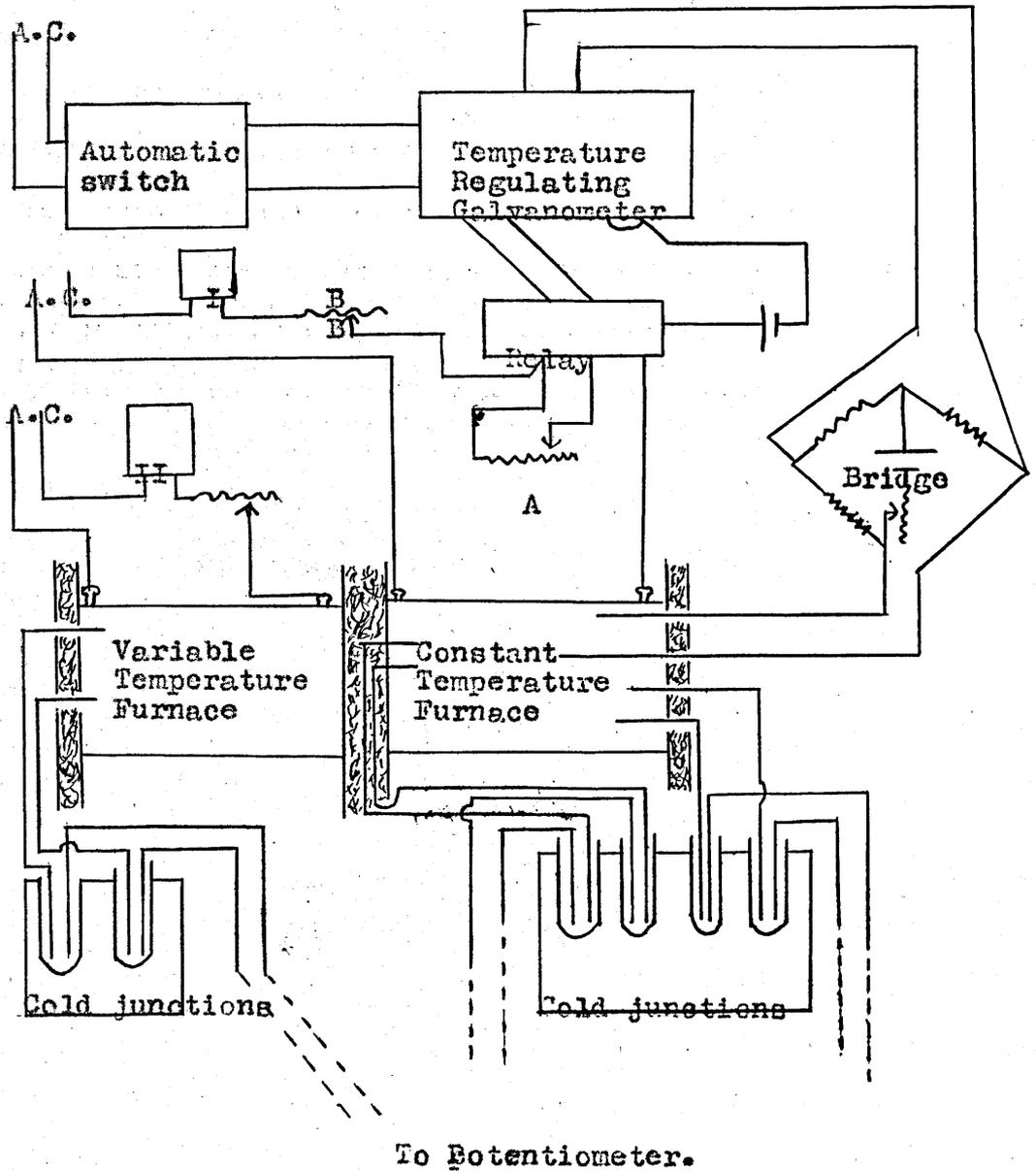
In contrast with the work done by Perrin on pure metals (*Annals de Physique*, Mai-Juin, 1920) in which he used an indirect method, a direct method was used in this work. Perrin measured the E.M.F. produced with change in temperature by using different pure liquid metals as one arm of a thermocouple and pure platinum wire as the other. Then by plotting, for instance, a liquid copper-platinum curve against a liquid tin-platinum curve derived the liquid copper-liquid tin curve.

In the present research the pure mercury and the alloys were used as separate arms of the thermocouple and the E.M.F.-Temperature relation found directly.

FURNACES

Two similar furnaces were used in this research. Each furnace consisted of a cast iron pipe about 6 cm. in diameter and 30 cm. long. Wrapped on the outside of each pipe was a layer of asbestos which was sealed to the pipe by water glass. On this layer of asbestos were then wrapped 60 turns of #24 chromel wire, the turns being spaced 5 mm. apart. Each end of the chromel

DIAGRAM OF COMPLETE APPARATUS.



- I. Ammeter
- II. Ammeter

wire was then fastened to the binding post at either end of the furnace, this binding post being insulated from the iron pipe in all cases. Around the pipe and coil of wire were then wrapped 6 layers of asbestos and sealed by water glass. Each furnace was then mounted on a brick, horizontally, by means of sheet metal bands.

An iron platform was permanently mounted in one furnace. It was 30 cm. long and $3\frac{1}{2}$ cm. wide so that it occupied the lower region of the furnace. On this platform were placed the two U-tubes, which will be discussed in detail later.

The second furnace had no platform in it. However, there was a coil of nickel wire 5 cm. in diameter and 16 cm. long which had been wound on a cylindrical piece of copper, the wire being insulated from the copper by means of asbestos. This coil was placed in the second furnace and kept from contact with the walls of it by means of pieces of glass tubing. The purpose of this coil was to regulate the temperature of the constant temperature furnace by means of a bridge circuit and galvanometer. The operation of this bridge circuit and galvanometer will be discussed in detail later. A snug pad of asbestos was placed between the two furnaces to keep heat from transferring from one to the other. Asbestos pads two inches thick were placed on the open end of either

furnace and the pads held in place and the furnaces held in close contact to each other by an adjustable wire extending around the furnaces and pads.

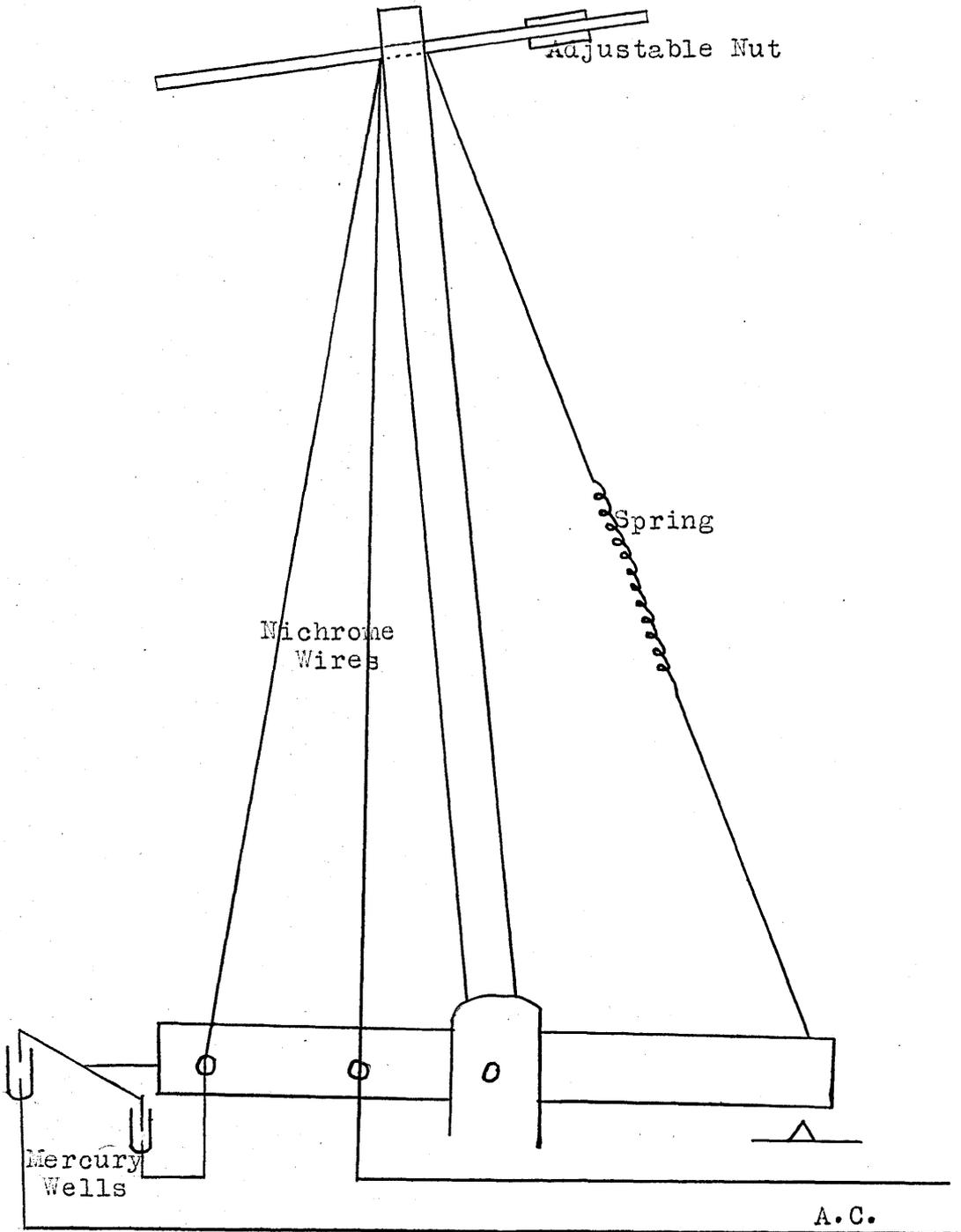
CONTROL OF CONSTANT TEMPERATURE FURNACE.

As one of the furnaces was to be kept at a constant temperature, a rather unique apparatus was devised to do this. The controlling device consisted of three separate parts which shall be called: (1). An automatic switch, (2). A temperature regulating galvanometer, and (3). A relay. These will now be discussed in turn.

AUTOMATIC SWITCH

The automatic switch consisted of an upright wood bar which was pivoted to a short horizontal bar which in turn was pivoted to the base of the apparatus so as to rock slightly back and forth. The upright boom was fastened to the horizontal boom on one side by an adjustable spring and on the other side by two strands of small nichrome wire. The horizontal bar made contact with two separate cups of mercury in the base of the apparatus by means of a U-shaped wire. In parallel with the mercury cup was a condenser, the purpose of which, was to reduce sparking at the break of the circuit. This piece of apparatus worked as

ENLARGED DIAGRAM OF AUTOMATIC SWITCH

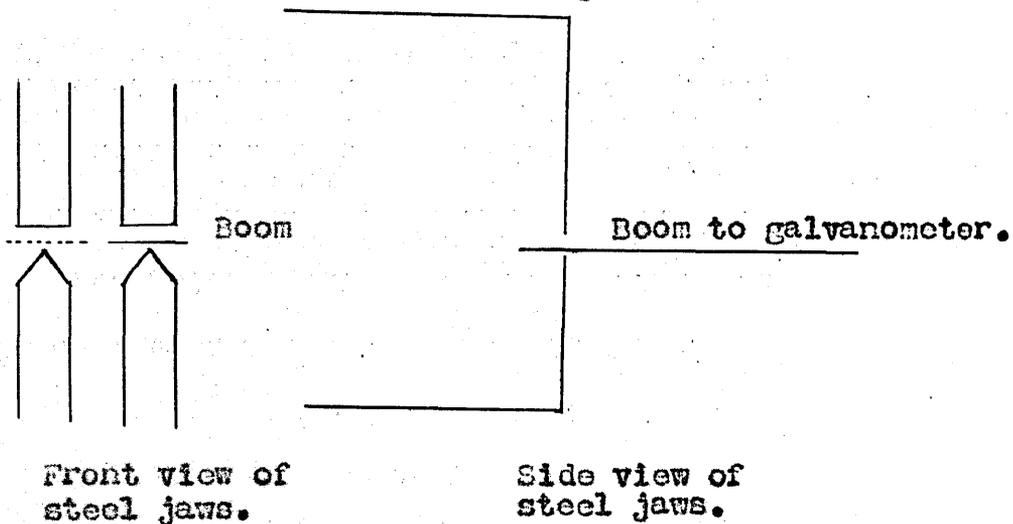


follows: A current through the two nichrome wires heated them causing them to expand, and as they expanded the adjustable spring pulled the upright boom over, thus breaking the circuit in the mercury cups. As the wires now cooled they contracted and pulled the boom over to its original position, thus again closing the circuit. The time for one oscillation of the upright boom was varied by the adjustable nut, as shown, and in operation was normally open for about 20 seconds and closed for 7 seconds. The connections to the mercury well and the horizontal were of small flexible wire in order not to interfere with the freedom of motion of the boom.

TEMPERATURE REGULATING GALVANOMETER

An important part of the apparatus was the temperature regulating galvanometer. A Leeds-Northrup type H portable galvanometer was used, but the galvanometer was considerably modified for the work. First of all a rigid steel frame was fastened to the tripod of the galvanometer extending to the front of the instrument 20 cm. and then upward at right angles about 12 cm. Mounted on this steel frame was a wood frame which could slide up and down the steel frame and be held in place by set screws. Mounted on this wood frame were four steel spring jaws, two to open upward and two to open downward.

The glass was taken from the front of the galvanometer and a celluloid boom with a paper tip was carefully fastened to the movable coil of the galvanometer, care being taken in all cases to allow the coil to swing freely. When the galvanometer was balanced this boom was perpendicular to the face of the galvanometer and hung between the two pairs of jaws so that no metallic contact was made as the jaws closed.



The upper pair of metal jaws rested on a fine nichrome wire but was insulated from it by small sections of glass tubing. This wire then circled an insulating knob on the wood frame and passed back over the pair of lower jaws but was insulated from them by glass tubing as mentioned above. The two ends of this wire were connected so as to make a complete series circuit with the automatic switch described above. Then as the automatic switch

closed, this nichrome wire heated and expanded allowing the jaws to close. The upper left hand jaw and the lower left hand jaw made metallic contact which closed an auxiliary circuit through the relay, but the right hand upper and the right hand lower jaw were kept separated by the paper boom. This boom travelled back and forth horizontally as the temperature and therefore the resistance of the nickel coil in the constant temperature furnace varied slightly. Therefore, the relay circuit is opened or closed as the case may be. Notice in the diagram of the complete apparatus that the terminals of the nickel coil are attached to the galvanometer.

RELAY.

The relay circuit is connected in parallel with the jaws of the temperature regulating galvanometer. Also connected in parallel with this relay is a variable resistance (A in the diagram of complete apparatus). If this variable resistance is shorted by the relay then the current through the constant temperature furnace is regulated by the rheostat B only. But if the variable resistance A is not shorted then the current is regulated by the combined resistance of A and B in parallel. By varying A and B, first by trial and error, currents could be obtained through the furnace which kept its temperature very constant as indicated by the resistance of the nickel coil.

In order for a relay to work as indicated, a special one was necessary. The one here used was the kind usually found on the thermostat of a heating plant. It was provided with a horizontal boom, one end of which made contact in two separate wells of mercury, by means of a U shaped wire, as the boom tipped down when the relay was closed through the galvanometer and tipped up as the relay was opened through the galvanometer. When the boom was down the current went through the U shaped wire and was therefore regulated only by the rheostat B mentioned above. But if the boom were up the current went through both A and B and was regulated accordingly.

Thus to review the complete process, the current passed through the automatic switch periodically. This in turn opened or closed the jaws of the temperature regulating galvanometer by heating or cooling the nichrome wires on which these jaws rested. This in turn controlled the relay as the paper boom passed back and forth between the jaws of the galvanometer as the resistance of the nickel coil changed. When the apparatus was working nicely this paper boom swung back and forth every five or seven minutes showing that the temperature of the coil was remaining very constant.

BRIDGE CIRCUIT.

The bridge used in this research was a Leeds-Northrup box bridge. The bridge was used not to measure the resistance of the coil but to balance it, i.e. to keep the temperature constant and therefore its resistance constant. There was a constant current through this bridge, the source of E.M.F. being one coil of an Edison storage battery. A resistance of 62 ohms was placed in series with the bridge to reduce the current through it and thus keep the coils from heating. The original resistance of the nickel coil was 3.2. ohms and rose to 6.0 ohms when the apparatus was being used in the taking of data. The measurements were taken on a 10 to 1 scale as results seemed more consistent.

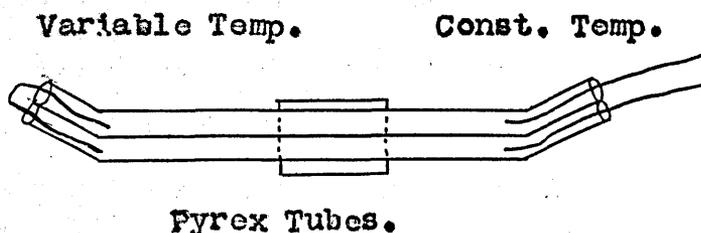
All readings of the E.M.F. developed in the thermocouples were taken on a Leeds-Northrup type K Student Potentiometer. An Eppley standard cell (E.M.F. 1.018 volts) was used as a standard and two dry cells were used as a working battery. Two variable resistance boxes were placed in parallel and used to help regulate the standard cell against the working battery. A Leeds-Northrup portable galvanometer was used with the potentiometer.

U-SHAPED TUBES.

Some means had to be devised to keep the alloys in a liquid state and at the same time use them as arms of

a thermocouple. Therefore, two pyrex tubes 15 mm. in diameter and 30 cm. long were bent up at each end and fastened together horizontally, side by side, leaving them 25 cm. long in the clear. The tubes were fastened to each other by means of tin clamps which were cut the shape of the furnace, so that when the tubes were in the furnace they were firmly in place.

These two tubes were placed on the platform in the variable temperature furnace and extended into the



nickel coil in the constant furnace for about 10 cm. Pure mercury was placed in one of the tubes and the alloy was placed in the other. These two metals were kept in metallic contact by a U shaped piece of nichrome wire with either end dipped into the liquid in the tubes. There was no apparent chemical action between the nichrome wire and the liquids after constant usage so it seemed safe and proper to use this wire. This wire was run through asbestos corks placed in the opening of each tube in order to reduce oxidation as much as possible. Leading from the other end of each tube, through an asbestos cork, was a piece of nichrome wire about one meter long. Thus, the two tubes when filled with metal, the U shaped wire, and the two wires comprised the liquid thermocouple.

COLD JUNCTIONS.

Two ice packs were used as cold junctions. These were tubes of mercury extending into thermos bottles filled with ice. These cold junctions were used to prevent the introduction of stray E.M.F. from a switch contact.

PREPARATION OF ALLOY

One of the most exacting parts of this work was the preparation of the alloys. Pure tin was obtained from the chemical supply room and the mercury was cleaned through filter paper and then distilled. The metals were weighed on a chemical balance. The tin was melted in a porcelain or pyrex dish, under paraffine, in order to keep the tin from oxidizing and also to prevent the tin from alloying with the metal dish. When the tin was melted the mercury was poured into the dish and the mixture was well stirred as it was solidifying in order to obtain a homogeneous mixture. In some cases the mixture was poured into the U-shaped tube before it solidified. In this connection I wish to say that I used some of the alloys prepared by J.M. Tevis who was working on the Thermal Conductivity of the same alloys.

FURNACE THERMOCOUPLES.

To record the temperature of the two furnaces, alumel-chromel thermocouples were used. These couples were calibrated by the usual method of measuring the

E.M.F. produced with the junction in tin at its solidifying point, in zinc at its solidifying point, and in steam at atmospheric pressure while the other end was in an ice pack at zero degrees centigrade. A base metal couple was used as it produces a larger E.M.F. than a rare metal couple and also the couple was used over a range in which it is known that the couple is very dependable.

In order to put these couples as near the point as possible whose temperature was to be measured and at the same time to have them at the same temperature as the point, two layers of sheet copper about 5 cm. wide were wound around the U tubes at this point and wired firmly to the tubes. A hole was drilled in the copper and a small glass tube dropped into it. The couples were bent at right angles near the end and dropped into the tubing, where it was held very firmly during the taking of data.

PROCEDURE

The final data were taken in the following manner. The U tubes were thoroughly cleaned each morning. In case the alloy did not flow it had to be melted and poured from the tube. The new specimen of alloy was placed in its proper tube and the pure mercury in its proper tube. The alloy was melted outside the furnace and well mixed as it was put in the tube. The U shaped wire

connection was then inserted with one end in each tube. The furnace thermocouples were placed in their proper places, the two furnaces placed end to end with the asbestos pad between them, the asbestos pads placed against each open end of the furnaces, and the whole apparatus wired securely together by the adjustable wire encircling it. In the meantime the four thermocouple wires, the leads from the alloy couple, and the leads from the nickel coil were brought out through their respective openings in the asbestos pads. All these lead wires were insulated from the walls of the furnaces by sections of glass tubing. The cold junctions were prepared and the current now sent through the apparatus. The process described here required from one to one and a half hours.

After considerable experimentation it was found if 4.8 amperes were sent through the constant temperature furnace while the automatic switch, temperature regulating galvanometer, and relay were connected as per diagram, that the constant temperature furnace would settle down at a temperature of 278 degrees centigrade after several hours. This temperature being sufficient to melt any alloy used and not being high enough to boil the mercury, it was decided to use this setting each day. About three amperes were sent through the varying temperature furnace and after two or three hours when equilibrium of heat had been established between the furnaces and the alloy in them, data

were taken. The working battery of the potentiometer was balanced against the standard cell before each reading was taken. The rest of the readings for the day were taken as the varying temperature furnace was allowed to cool very, very slowly, the other furnace being kept constant. Some of the data were taken as the varying temperature furnace was allowed to heat very, very slowly. On the average probably three hours elapsed between successive readings. The only modification of the above process was that an alloy of different percent of tin in mercury was used against mercury each day.

Chief among the difficulties encountered in taking data were: 1. Control of constant temperature furnace. Although the automatic switch was used to do this, still it required adjustment before it would function properly. The first attempt was to keep the temperature slightly below the boiling point of mercury, possibly around 330 degrees centigrade. However little success was had so the attempt was made to keep it about 300, but without success. Finally it was discovered the furnace would remain stationary at 278 centigrade. Therefore, this temperature was used in the work.

2. Bridge circuit. The bridge had a constant current through it and the coils of it seemed to heat especially after it had been used for some hours, and allowed the constant temperature furnace to vary. But by

inserting a 65 ohm coil in series with the bridge circuit the heating of the coils was greatly reduced and the difficulty remedied.

3. Thermocouples. Various devices were used to hold the thermocouples in their proper place. Asbestos cord and wire were used but with no success. Finally, as mentioned above the couples were held in place by copper strips.

4. Solidification of alloys. On several occasions the alloy would solidify in the tube while the rest of the apparatus was being assembled for the day's experiment. In this case the mixture would not be a homogeneous one and the resulting data would be very erratic. Therefore, the furnaces were kept heated sufficiently to keep the alloy melted while the apparatus was being assembled. While it was inconvenient to work with the hot furnaces, still it overcame the difficulty.

5. Heat transference. Trouble was encountered early in the work by heat travelling from one furnace to the other. However, this seemed to be effectively overcome by cutting pads of asbestos to fit snugly over the U tubes as the furnaces were placed end to end.

6. Air currents. Paste board boxes were placed over the automatic switch and the temperature regulating galvanometer so air currents would not molest their action.

Percent by weight Hg. Tin		Percent atomic Hg. Tin		Temp. of variable furnace	Temp. of constant furnace	Diff. in temp.	M.V. by Hg-Tin couple
0	100	0	100	232 C	278 C	46	.315
0	100	0	100	222 C	278	56	.45
0	100	0	100	188 C	278	90	.82
0	100	0	100	208 C	278	70	.55
50	50	37	63	167 C	278	111	.785
50	50	37	63	190 C	278	88	.63
50	50	37	63	215 C	278	63	.44
50	50	37	63	245 C	278	33	.227
50	50	37	63	262 C	278	16	.090
70	30	58	42	233 C	278	45	.30
70	30	58	42	196 C	278	82	.54
70	30	58	42	184 C	278	94	.605
75	25	64	36	216 C	278	62	.375
75	25	64	36	148 C	278	30	.18
75	25	64	36	251 C	278	27	.16
75	25	64	36	248 C	278	20	.115
84	16	75	25	218 C	278	60	.33
84	16	75	25	196 C	278	82	.50
84	16	75	25	183 C	278	95	.53

Percent by weight Hg. Tin	Percent atomic Hg. Tin	Temp. of variable furnace	Temp. of constant furnace	Diff. in temp.	M.V. by Hg. Tin couple.
90 10,	84 16	229 C	278	49	.245
90 10	84 16	256 C	278	22	.107
90 10	84 16	267 C	278	11	.05
90 10	84 16	154 C	278	124	.63
96 4	93 7	248 C	278	30	.137
96 4	93 7	223 C	278	55	.1245
96 4	93 7	206 C	278	72	.325
98 2	97 3	246 C	278	32	.12
98 2	97 3	240 C	278	38	.15
98 2	97 3	233 C	278	45	.17
98 2	97 3	228 C	278	50	.20
98 2	97 3	189 C	278	89	.36

The thermoelectric power equals dE/dT , i.e. the slope of the tangent of the curve representing the change in E.M.F. per degree difference in temp.

The thermoelectric power of each alloy taken from plate

II is.

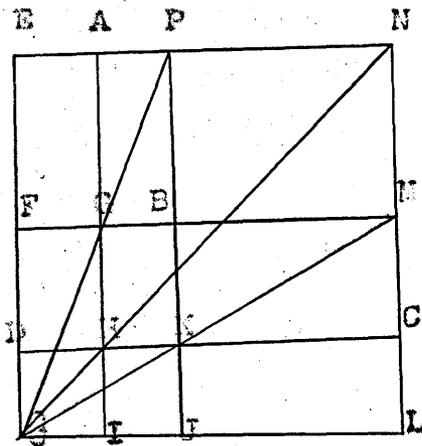
100% Tin vs. Pure mercury	----	.800
50% Tin vs. Pure mercury	----	.710
30% Tin vs. Pure mercury	----	.655
25% Tin vs. Pure mercury	----	.605
16% Tin vs. Pure mercury	----	.560
10% Tin vs. Pure mercury	----	.510
4% Tin vs. Pure mercury	----	.455
2% Tin vs. Pure mercury	----	.400

DISCUSSION OF DATA.

Three points lie on a rectangular hyperbola if the diagonals of the rectangles formed on the points, sides parallel, intersect in a common point.

Given: Any three points A, B, C with the three rectangles APBG, BECK, and ANCH constructed on them.

To prove: That the three diagonals PG, MK, and $\frac{AN}{HN}$ intersect at O.



Extend AP to E and N, GB to F and M, CK to H and D
 Now rectangles OEAI and OFBJ are equal, because
 triangle OEP equals triangle OPJ
 triangle GAP equals triangle GBP
 triangle OFG equals triangle OGI
 so OEAI equals OEP minus GAP plus OGI and OFBJ equals
 OPJ minus GBP plus OFG.

Therefore, rectangle OEAI equals OFBJ.

A similar proof holds for OFBJ and ODCL. And as
 area of each equals the product of the x, y, values
 it contains, xy equals a constant for each point.

Moreover, the diagonal NH of rectangle ANCH may be seen to intersect at O. The rectangle ONEL is bisected by ON. H is the intersection of rectangle OEAL and rectangle ODCL and lies on the diagonal ON, for subtracting, already proved equals OEAO from triangle ONL and OHLO from triangle ONL leaves Equals. This being the case, the line NH must bisect HANC and be its Diagonal.

The above construction was used to determine if the curve of the Thermoelectric Power versus the Percent, by weight of tin was a rectangular hyperbola. It was found not to be. If it had been it would have indicated a possible relation between the thermoelectric power and the electrical conductivity of the alloys used, as G.V. Emery in his Thesis (University of Kansas, 1924) found the curve of Electrical Conductivity versus the same mercury-tin alloys to be a rectangular hyperbola.

However, as there was a similarity between the two above mentioned curves, the thermoelectric power was plotted against the Relative Conductivity (Electrical) for corresponding percents of tin in mercury, as shown in Plate IV of this work. The Electrical Conductivity of mercury was taken as Unity.

This curve shows indications of being a straight line. Especially is this true in the region of 3% tin

in mercury to 100% tin. However there must be a decided break in the curve somewhere below 3% as the curve must go through the origin (as indicated by the dotted line), because the thermoelectric power of mercury against mercury is zero.

CONCLUSIONS.

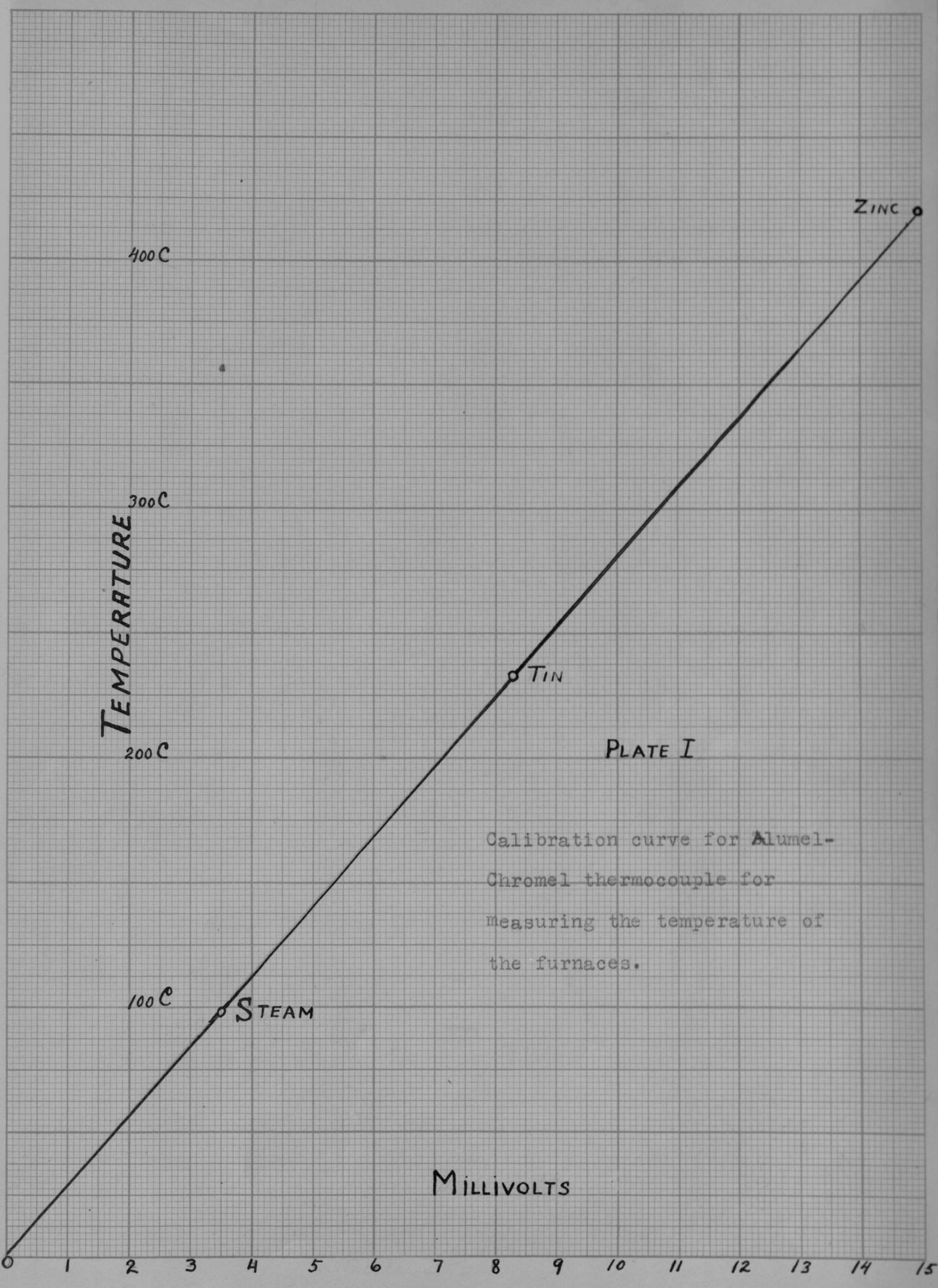
In this research it has been established that a linear relation exists between the E.M.F. and the Difference in Temperature for mercury-tin alloys of different concentrations used as one arm of a thermocouple and pure mercury as the other.

The greatest variations in the thermoelectric power was found in the cases of small percent of tin in mercury. It is worth noting that a 8% tin-98% mercury had a thermoelectric power of .40 while pure tin had a thermoelectric power of .80, when each was used with pure mercury as the other arm of the thermocouple.

No definite relation has been drawn from Plate IV, however it appears that some simple relation exists between the Thermoelectric Power and Electrical Conductivity of mercury-tin alloys at least in the region from 3% tin in mercury to 100% pure tin. Additional experimentation is necessary in order to determine the nature of the curve

for alloys of less than 5% tin in mercury.

In concluding this report the writer wished to express his sincere thanks to Dr. C.V.Kent for his constant interest, assistance, and suggestions in the work, and to Dr. E E.Kester and Staff for the splendid assistance and cooperation in securing the necessary apparatus and supplies.



MILLIVOLTS

- 1. 100% Tin vs. Pure Hg.
- 2. 50% Tin-50% Hg. vs. Pure Hg.
- 3. 30% Tin-70% Hg. vs. Pure Hg.
- 4. 25% Tin-75% Hg. vs. Pure Hg.
- 5. 16% Tin-84% Hg. vs. Pure Hg.
- 6. 10% Tin-90% Hg. vs. Pure Hg.
- 7. 4% Tin-96% Hg. vs. Pure Hg.
- 8. 2% Tin-98% Hg. vs. Pure Hg.

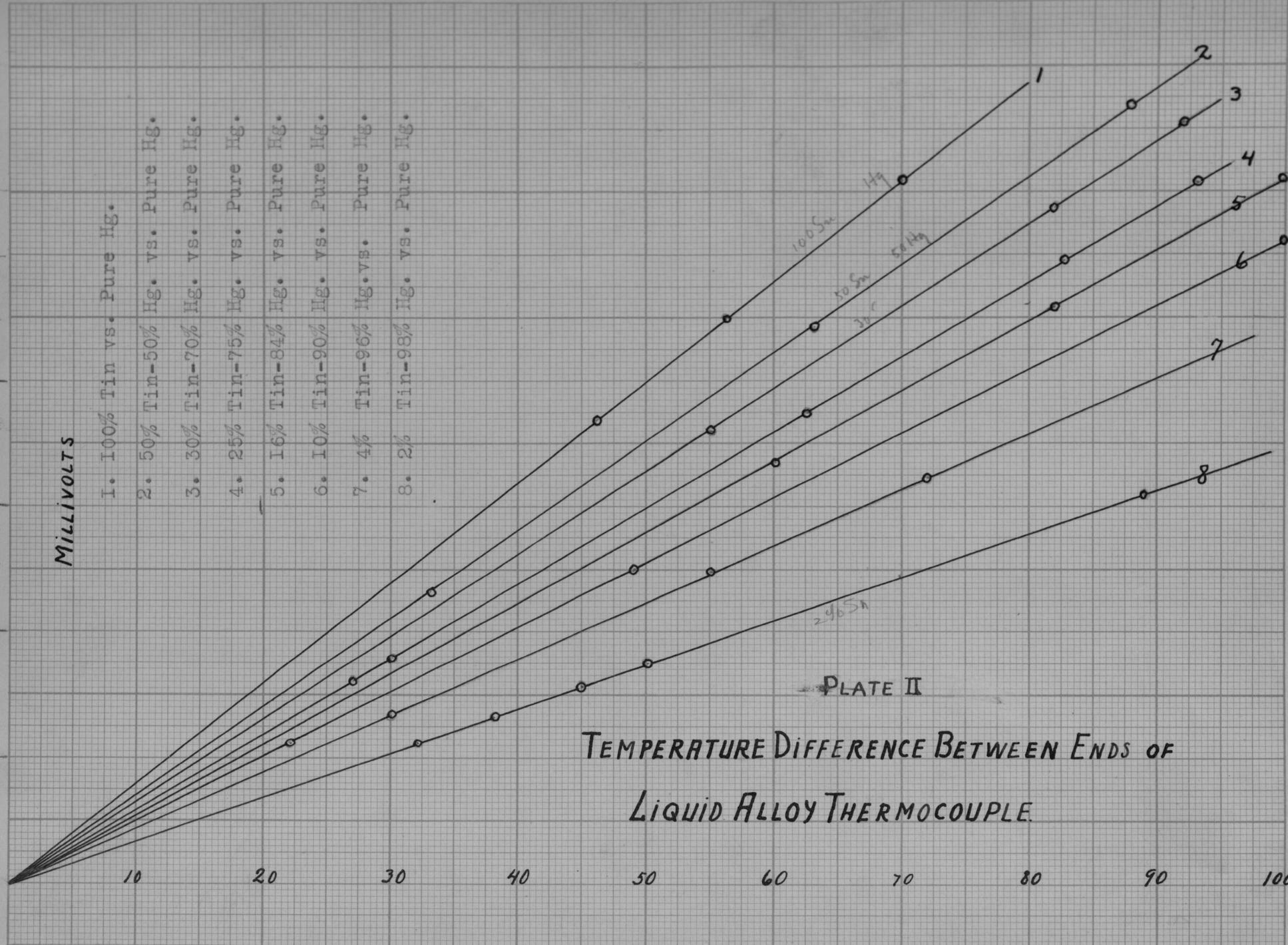
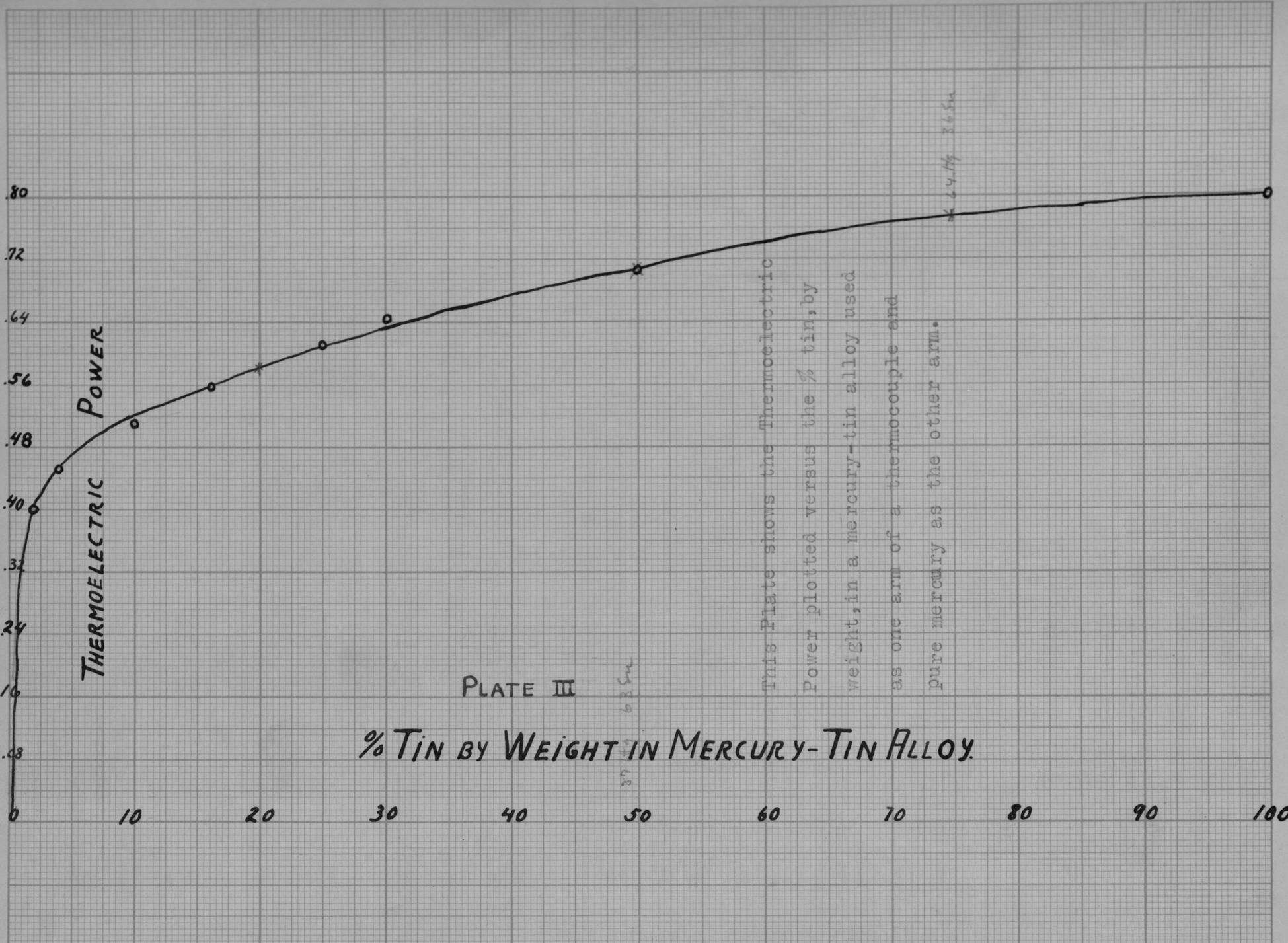


PLATE II

TEMPERATURE DIFFERENCE BETWEEN ENDS OF
LIQUID ALLOY THERMOCOUPLE



THERMOELECTRIC POWER

PLATE III

% TIN BY WEIGHT IN MERCURY-TIN ALLOY

This Plate shows the Thermoelectric Power plotted versus the % tin, by weight, in a mercury-tin alloy used as one arm of a thermocouple and pure mercury as the other arm.

0.7
0.635m

0.64
0.44
0.65m

