

ELECTRICAL RESISTANCE AND THERMO-ELECTRIC
POWER OF THE ALKALI METALS¹

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ABSTRACT

Electrical resistance and thermo-electric power of the five alkali metals, -183°C to 250°C .—Pure samples of the metals were fused into glass or quartz tubes, and measurements were made by means of thermo-junctions sealed into each end. Enough points were secured in each case to determine the slopes and the breaks in the curves. In both the resistance and thermo-electric power lines, changes of slope are observed beginning gradually 100 degrees or more below the melting point. These are taken to indicate *transformations* in each case from an α to a β form. These transformations occur at approximately the temperatures, 50°C for Li, -20°C to $+20^{\circ}\text{C}$ for Na, -120°C for K, -35°C for Rb, and -80°C for Cs. In all cases a sharp rise in thermo-electric power and resistance occurs as the melting point is approached. The *temperature coefficients* of resistance decrease smoothly with increasing atomic weight for all forms.

Atomic heat of electrons in the alkali metals.—The atomic heat of electricity as computed from thermo-electric data is approximately 0.24 cal. for Na and K, and 0.58 cal. for Rb and Cs. The values are too small to account for the observed excess of the atomic heats for these metals above the equipartition value.

INTRODUCTION

BEFORE any theory of electrical conduction can be regarded as being most consistent with the facts or as most clearly explaining observed behavior, more complete knowledge of the actual behavior of pure materials should be at hand. It has seemed to the writer that our knowledge of the experimental facts of electrical conduction is very meager. Our knowledge of the change of electrical resistance with temperature is quite fragmentary. With the so-called metallic conductors we have a positive temperature coefficient, and with the non-metallic conductors a negative coefficient. With certain intermediate elements (metalloids) the coefficient is positive or negative depending upon the temperature. A search of the literature reveals the fact that only in a few isolated cases have sufficient data been taken on pure materials over wide temperature ranges to warrant positive statement of the resistance law. The observations at the Leiden laboratory have given us for a number of metals most accurate and extended data over the low temperature

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range but there is need of data on many more metals and non-metals widely distributed over the Periodic Table.

In the present studies on the alkali metals² measurements of thermo-electric power were made through certain temperature ranges simultaneously with the resistance measurements, or as nearly simultaneously as was consistent with the requirement of a uniform temperature over the specimen for the resistance measurement and the establishment of a temperature gradient for the thermo-electric power reading. There is considerable evidence that the relation between thermo-electric power and temperature for a pure material in a given crystalline modification is expressed by a straight line and that a change of slope occurs only when the material undergoes a transformation. If this may be assumed, the thermo-electric power line gives a means of detecting changes in crystalline structure. The present work is the first contribution in a systematic study of the resistance temperature relation for pure elements, the plan being to study the elements group by group throughout the Periodic Table. Resistance curves for the five alkali metals on specimens of very high purity together with the thermo-electric power lines have been obtained. The measurements were carried from liquid air temperatures over a range of 400° or more, in all cases through change of state, with observations on the liquid state.

METHODS EMPLOYED IN THE PRESENT WORK

It was the aim of the writer to secure resistance measurements at temperatures sufficiently close together to establish definitely the resistance-temperature relation, and to secure thermo-electric power data on the same specimen simultaneously, so that collateral information might be at hand of possible transformations which might account for peculiar behavior of the resistance lines.

Because of the great chemical activity of these metals, special technique is required in their manipulation. Caesium, rubidium, and lithium were reduced by the writer from c.p. chlorides specially prepared by Dr. J. Papish of the Chemistry Department, Cornell University. Spectroscopic tests of both the salts and the metals were also made by him. Except in the case of lithium the metals were run into lead glass capillary tubes through the walls of which were fused two pairs of fine platinum wires about two inches apart. In the case of caesium and rubidium, the tubes were sealed off in vacuo; potassium and sodium were handled under "nujol," a mineral oil mentioned by Bridgman as especially good for this purpose. One wire of each pair was cut off close to the glass and

² A summary of previous work on the alkali metals is given at the end of this paper.

a constantan wire soldered to it. The arrangement is shown in Fig. 1. The platinum and constantan wires of each junction were of sufficient length to extend to a Dewar cylinder where they were connected to copper leads. The contacts with the copper wires were kept at the temperature of melting ice. The platinum-constantan contacts were made through the metal inside the capillary tubing. Temperatures at the two points in the metal could be determined by connecting the junctions in turn to the potentiometer.

The platinum-constantan junction was adopted after considerable experimentation as especially suitable for the low temperature range (0° to -180°), where the platinum-platinrhodium junction is inoperative. Platinum-constantan was found at least as reliable as iron-constantan and eliminated a soldered joint on one of the wires of each pair. To

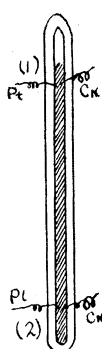


Fig. 1

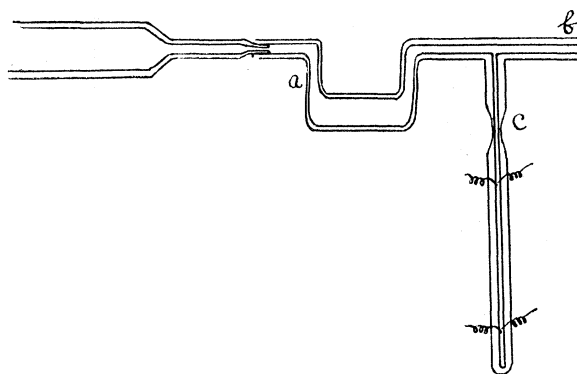


Fig. 2

measure resistance, current was sent in from a storage battery by way of the constantan wires and the fall of potential measured by means of the platinum leads. Before and after such readings temperatures were checked at the two junctions.

The current was measured by determining the fall in potential across a standard Hartmann and Braun resistance in series, whose value was either 0.01 or 0.001 ohms. For thermo-electric measurements a temperature gradient was established along the specimen, the temperatures measured at each end, and the electromotive force between the platinum leads determined. A temperature difference of from six to ten degrees was found most suitable for accurate work. The value of this difference could be determined to within 0.05° , whereas the actual temperature at either end was not known better than about $\pm 0.5^{\circ}$. Potentiometer readings were good for three decimal places in temperature, which was beyond the accuracy of the calibration. Our knowledge of the

fixed points and the need of interpolating between such points necessitated discarding two of the potentiometer figures as not significant as regards actual temperature, but the decimal places are significant in taking the difference between two temperatures close together. The difference as given by the potentiometer, divided by the slope of the calibration curve at the point, i.e., by the thermo-electric power of the platinum-constantan junction at the temperature in question, gives the temperature difference with very high accuracy, at least that indicated above. The thermo-electric power as thus computed was plotted against the mean of the temperatures of the two junctions. The potentiometer used throughout was an Otto Wolff low resistance instrument.

For the calibration of the platinum-constantan couple, liquid air that had been boiled violently for several minutes was taken as giving the boiling point of liquid oxygen, viz., -183°C , carbon dioxide snow and ether as -78°C , mercury freezing point as -40°C , and fairly good points supported by readings of a Reichsanstalt pentane thermometer, viz., the melting point of ether -117°C , of acetone -94.6°C , and of chloroform -65°C . The gap between -117° and -183° is covered by interpolation based upon the constants of the equation for the junction as determined from the known points. Above the ice temperature there are numerous good fixed points.

TEMPERATURE BATH AND CONTROL

The capillary tube containing the metal was placed in an outer protecting glass tube. This was encased in a heavy brass tube whose walls were about $\frac{1}{4}$ inch thick. Resistance measurements were first made at the temperature of melting ice. These readings were repeated as a check before and after every "run" or set of observations. The specimen with the leads emerging from the top of the brass tube was packed in wool and lowered into a large Dewar cylinder where it was completely immersed in liquid air. Resistance measurements were taken at this temperature and then the specimen was raised in the flask until it was entirely above the surface of the liquid. The space around the specimen and above it for about six inches was packed tightly with wool. Through this packing a glass tube extended to the bottom of the cylinder. Liquid air was sprayed through the wool from above until both junctions were steady at -183°C . The specimen thus packed was then allowed to stand, whereupon its temperature slowly rose, that of the upper junction slowly drawing away from that of the lower and slowly increasing the temperature gradient along the specimen. If the difference became greater than twelve or fifteen degrees, air was blown through the glass

tube, thus forcing the cold air from the bottom up through the wool, lowering of course the temperature of the specimen as a whole but also reducing the temperature difference. It was found that by continuing this stream of air up from the bottom, the two junctions could be brought to the same temperature reading. If the air stream were continued until no liquid air remained and then was cut down to a very slow current the temperature of the two junctions could be maintained alike as the specimen slowly heated to room temperature. On some runs four hours or more were required for the rise from -183° to 0° . By cutting down the air stream or shutting it off a temperature difference would develop and this difference could be quite satisfactorily controlled by the air stream. Many of the resistance measurements were made with the temperature difference reduced to zero but probably a majority were taken when still three or four degrees difference existed over the length of the specimen. The value obtained was plotted against the mean. Such values were found to fit the curve and to duplicate points obtained with the greater time and trouble required for uniform temperature. Thermo-electric power readings were taken with any temperature difference between 2° and 20° or more (in some cases). Since temperatures were slowly changing, readings were taken in the order, e.m.f. across specimen, top junction, bottom junction, top junction, e.m.f. across specimen. The change in the two readings for the top junction was usually of the order of a few tenths of a degree and the average was taken. Usually the initial and final e.m.f. readings were unchanged. The heavy tube served to equalize the temperatures and apparently to produce a uniform gradient along the specimen. Without the brass casing the gradient rapidly became large and the data when plotted proved to be quite erratic. The brass tube made the difference between success and failure in getting consistent, reproducible thermo-electric power data.

For temperatures above room temperature, the Dewar was replaced by a tubular, spirally-wound, electric furnace. The temperature gradient was controlled by raising or lowering in the furnace. The resistance measurements were checked by observations in constant temperature baths of boiling ether, chloroform, alcohol, water and anilin.

CAESIUM

This metal was prepared by heating the c.p. chloride with pure metallic calcium in vacuo, the charge being placed in a long pyrex tube. On heating to about 400°C the reaction sets in, causing a glow to extend throughout the mass with condensation of caesium metal in the cooler

part of the tube. This was driven along the tube, redistilling at temperatures much lower than that of the reaction, the redistillations serving to purify the metal. The pyrex tube was finally sealed off separating the metal from the non-volatile materials in the hot end of the tube but still leaving it connected to the pump. To the pyrex tube was connected by means of thick-walled rubber tubing a lead glass tube containing an enlargement for receiving the metal. Between the enlargement and the pump was connected the glass capillary containing the platinum leads. The arrangement is shown in Fig. 2. The capillary and chamber were next well heated with a Bunsen flame while further exhaustion was carried on. The tube was then sealed off at *b* and the molten metal allowed to run into the lead glass chamber from the pyrex tube and the tube sealed off at *a*. The metal was then allowed to run into the capillary. The tube was filled very nicely on the first trial, as shown by good contacts at all leads. The capillary was finally sealed off at *c*, leaving space above the metal for expansion. The metal remaining in the enlargement was used for determination of melting point and for spectroscopic tests of purity. The tests indicated a trace of sodium as the only impurity. The melting point was found by immersing in water whose temperature was varied until the metal on agitation showed pasty condition. The average of many determinations which agreed closely was 27.4°C. Melting points for caesium tabulated in Landolt-Börnstein vary from 25.30 to 28.2°, the latter being the latest and presumably the most accurate value.

Resistance measurements at 0°C gave initially 0.01538 ohms. After immersing in liquid air and taking a number of preliminary observations at low temperatures the 0° reading was found to be 0.01530. Two sets of observations were then made over the range from 0° to -192°, giving the data shown graphically in Fig. 3. The resistance at 0°C after these runs was still 0.01530. After standing for two days the resistance at 0°C was found to be 0.01500. Observations were then made on the molten metal. After heating to 97°C and back, the 0°C reading was found to be 0.01503. Two sets of observations were then made in the range 0°C to 98°C. Above 98°C the specimen became blackened through reaction with the lead glass tube. Thermo-electric power measurements were made during these runs in the manner already indicated. The results are also shown in Fig. 3. The break in the thermo-electric power line at -80°C indicates presumably a molecular rearrangement or modification of some sort. The graph shows the ratio of the resistance at any temperature to that at zero. Specific resistance was not determined. The resistance relation is linear between -190°C and -80°C.

Between -80°C and 0°C a marked curvature indicates a different law. The resistance points by themselves do not conclusively bring out the change at -80°C but in connection with the thermo-electric power line the meaning of the deviation of the resistance points from the straight line followed up to -80°C is apparent. Above 0°C the metal apparently shows evidence of the approaching fusion. This behavior on approaching the melting point is characteristic of all the alkali metals as will be noted in the other curves. It suggests a gradual loosening up of the crystalline structure, the lattice however holding together and retaining the metal in the solid state until the complete collapse at the

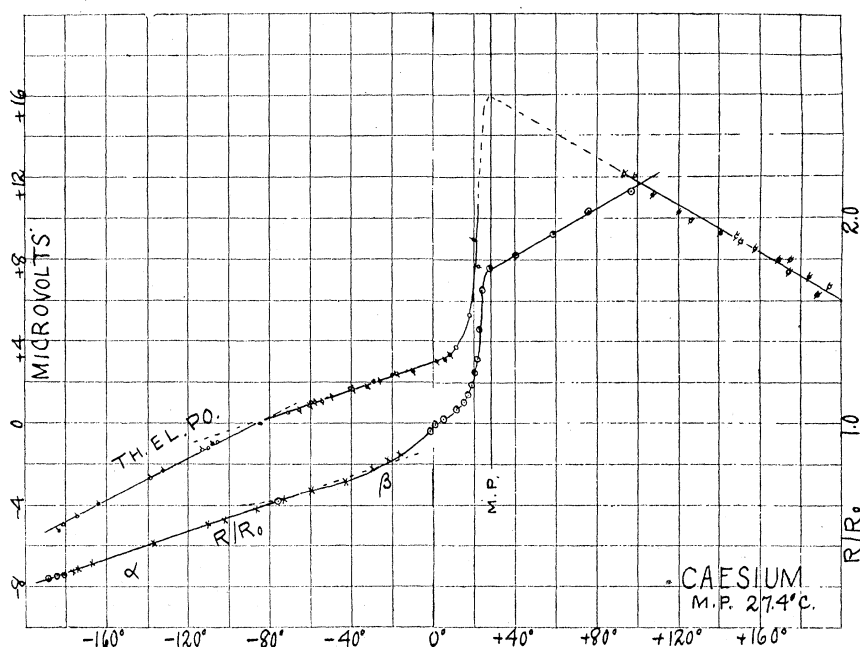


Fig. 3. Curves for caesium, m. p. 27.4°C .

melting point. The very great increase in thermo-electric power and resistance occur while the metal is solid. A very careful study of a sample of the metal in the evacuated tube showed the solid state with no evidence of pasty condition until at least 27.0°C was reached, whereas the changes in thermo-electric power and resistance are noticeable as far back as $+12^{\circ}\text{C}$. On cooling there is no such gradual change on approach to the melting point. The change sets in abruptly, the decrease in thermo-electric power and resistance being extremely sharp at first, although the final condition is apparently not reached for fifteen degrees or more below the melting point. The exceptional purity of all of these metals,

as indicated both by spectroscopic tests and by the melting points, makes it rather unlikely that the gradual changes on approach to the melting point from below are due to impurity. The freezing point in all cases was sharp but the loosening up of the lattice in the solid seems to start many degrees below the melting point. A number of cooling curves were taken on potassium. The change was absolutely abrupt at 62.5° . It is regretted that slow heating curves were not taken on some of these metals to test the abruptness of the melting. Bridgman is positive that premature rounding of the melting curve is an indication of impurity. A further investigation of this point is planned. It should be pointed out however that the curves shown are not melting curves and that the material is not in an unstable condition in this region where the lines are curving. The existence of two modifications, an α form, stable at low temperatures, and a β form, at higher temperatures, seems to be characteristic of the whole alkali group as will be noted from the curves.³

For molten caesium, the thermo-electric power and resistance lines were perfectly straight. The initial resistance run to 98°C gave a somewhat greater slope (temperature coefficient) than a run after observations on thermo-electric power to $+200^{\circ}\text{C}$ had been carried out. Resistance measurements made on the slow cooling from 200°C gave a straight line with slightly less slope. As the specimen had become completely blackened through reaction with the lead glass, the initial readings to 98°C were taken as giving the better value of the temperature coefficient. The temperature coefficient was changed by this slight contamination from 0.00260 to 0.00240.

RUBIDIUM

The rubidium was reduced from the chloride with calcium in vacuo and the same procedure followed as with caesium. Several attempts were necessary before the metal was finally obtained in the capillary with good contacts at the leads. The material used in the first trials had to be worked over and in this process suffered contamination, for the specimen as finally successfully mounted was found on later spectroscopic tests to

³ Note added February 1, 1924.—X-ray diffraction patterns recently obtained by the writer on lithium at various temperatures show a gradual fading out or obliteration of the lattice structure above the transformation temperature here reported, the β form therefore being the amorphous form. This is in agreement with the previously known fact that sodium is nearly amorphous (shows little or no x-ray diffraction pattern) at room temperature but is a body-centered cube at liquid air temperature, also with the fact that potassium shows no pattern at room temperature, while a clear pattern, body-centered cube, is obtained at liquid air temperature (Hull, *Phys. Rev.* **10**, 661, 1917; McKeehan, *Proc. Nat. Acad. Sci.* **8**, 8, 1922).

have considerable impurity of potassium. The melting point of this sample was found to be only 33.0°C . Thermo-electric power and resistance of this specimen, rubidium (1), are shown in Fig. 4. A second sample, rubidium (2) was spectroscopically pure and its melting point satisfactory, 37.2°C . Thermo-electric power and resistance are shown for this specimen, Fig. 5. The melting points, as reported by Landolt-Börnstein, for rubidium are 37.8°C (Eckard 1900) and 38.5°C . (Erdmann and Köthner 1896). The specimen, rubidium (2), was lost on the first attempted run through the melting point, the expansion cracking the glass tube. Since there was such a fair general agreement between

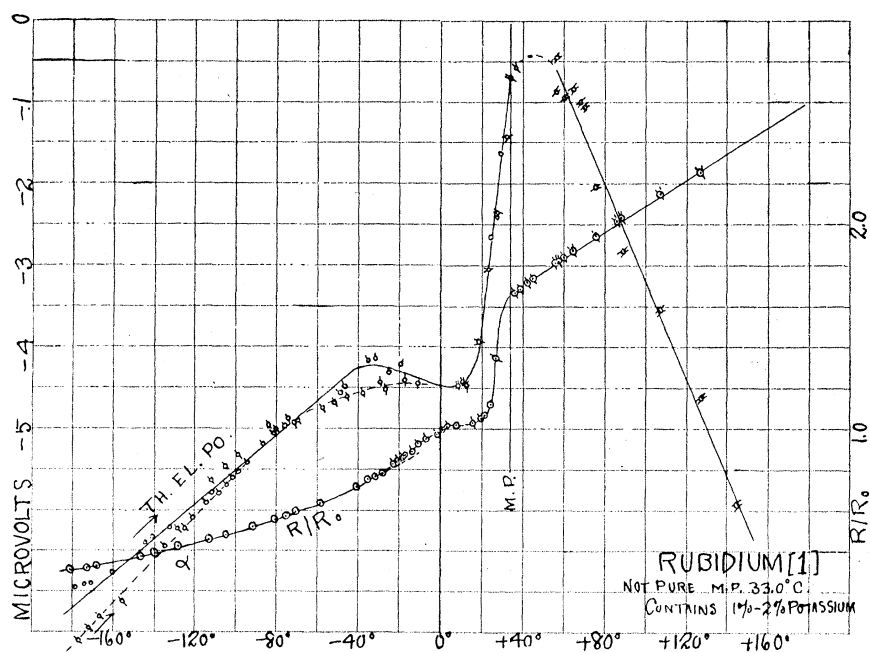


Fig. 4. Curves for rubidium containing 1 to 2 percent potassium.

the curves for the impure specimen and those for the better one and since data were obtained on the impure specimen through fusion and on the liquid metal as far as 150°C , a further attempt to check up the data on the liquid metal with a purer specimen was not made. The metal was found to possess α and β modifications, the transformation occurring at about -30°C .

The behavior on approach to the melting point is similar to that of caesium. The change in the resistance reading at 0°C for specimen (1) after cooling to liquid air temperature was 0.8 per cent. After melting and heating to 75°C and again cooling the resistance at $+20^{\circ}\text{C}$ had changed

from 0.0146 to 0.0156 ohms. Due to the formation of cavities on freezing it is not to be expected that the values of the resistance in the solid state will be repeated after melting. If the value at 0°C is redetermined however, the values of R/R_0 should repeat. This they did satisfactorily. The value selected for R_0 for the ratio R/R_0 for the liquid state was the lowest observed value, the value in which the effect of cavities on the mean cross-section was least. This value effects only the computation of the resistance change on melting and does not enter into the computation of the temperature coefficient. With specimen (2) the change in

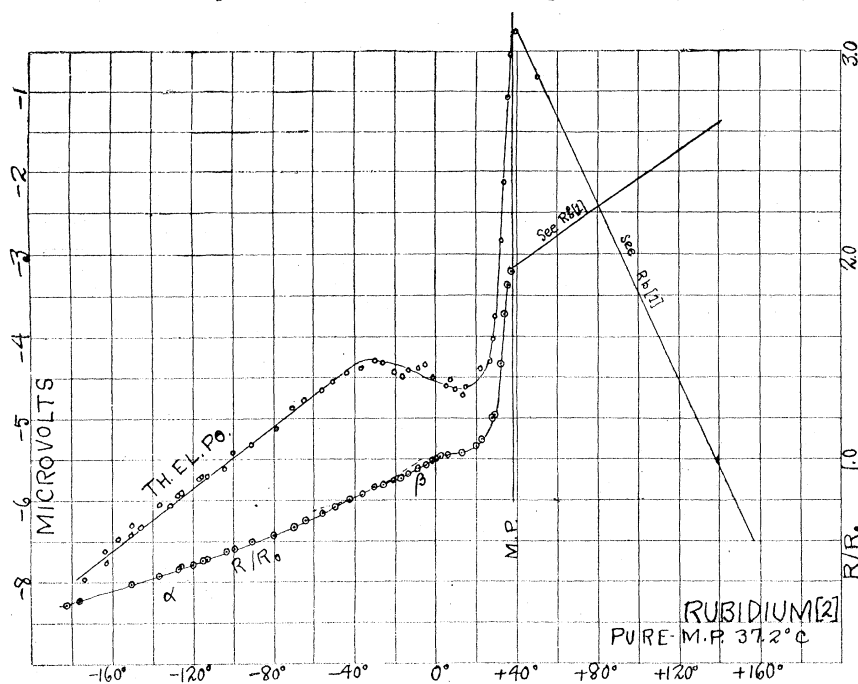


Fig. 5. Curves for pure rubidium, m. p. 37.2°C .

the value at 0°C after taking the low temperature readings was about two per cent. The mean value of R_0 was used for the ratio R/R_0 .

In plotting all curves large circles were used for resistance and small circles for thermo-electric power. Circles without tails indicate the first run. Circles with one tail, the second run; two tails, the third run, etc. The extent to which the various runs repeat can thus be noted.

POTASSIUM

The potassium metal was from old stock. The source was not known. Spectroscopic tests indicated high purity, the only impurities detected being traces of sodium and calcium. The melting point was 62.5°C .

This point was checked by means of differential cooling curves with thermo-junctions in potassium and aluminium. Very sharp, clear values were thus obtained with no variation whatever. 62.5°C agrees with the best values published for pure potassium.

It was not necessary to mount the specimens in vacuo. The molten metal, kept under "nujol" was drawn up into capillary tubes by suction, allowed to freeze, and the ends plugged with alundum cement and water glass to prevent running out when liquid. The curves, Fig. 6, indicate α and β modifications of the solid, the transformation occurring at about -120°C . Specimen (1), in which the heating was more rapid than

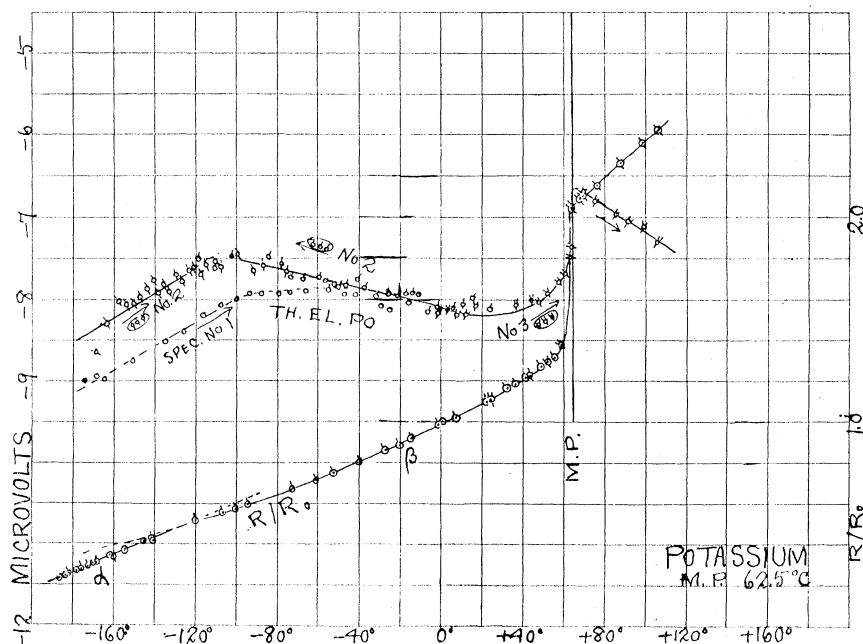


Fig. 6. Curves for potassium, m. p. 62.5°C .

with specimen (2), showed a rather gradual transition from the α to the β form. With specimen (2) the heating was very much retarded. The transition in this case appeared much sharper, occurring at about -110°C . The resistance line clearly indicates a change at about this point. The behavior on approaching the melting point is similar to that of caesium and rubidium. For specimen (1) the resistance at 0°C changed after the low temperature observations from 0.00700 to 0.00710. The zero value was unchanged after a second cooling to liquid air temperatures. After heating to $+55^{\circ}$ and cooling again to 0° the resistance changed from 0.00708 to 0.00697. After readings were taken

on the molten metal to 105°C the zero resistance was found to have increased to 0.00725. The specimen became blackened at this latter temperature. Repeated runs on the liquid metal gave parallel thermo-electric power lines slightly higher on successive runs, probably the effect of contamination.

SODIUM

A sample of very pure sodium was obtained from Professor L. M. Dennis of the Department of Chemistry. Spectroscopic test showed only a trace of calcium. The melting point was determined as 97.0°C. The values given in Landolt-Börnstein agree at 97.5°C. Specimens were prepared for measurement following the procedure employed for

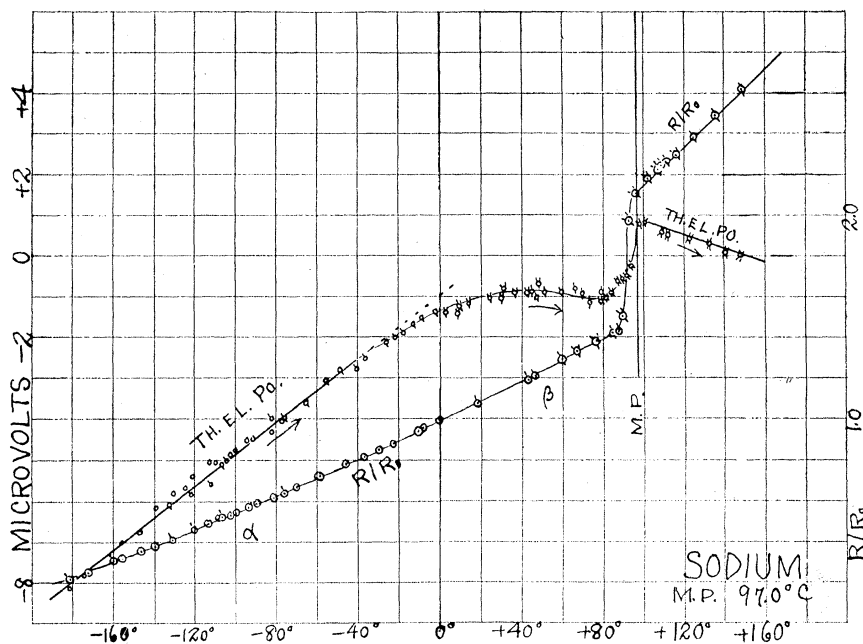


Fig. 7. Curves for sodium, m. p. 97.0°C.

potassium. The initial resistance at zero was 0.00755. After liquid air readings the value was 0.00753. After heating to +88° and back the value was 0.00752. After melting and heating to +150°C the zero value was 0.00760. Above -40°C, Fig. 7, the thermo-electric power points begin to deviate from the straight line followed from -180°C, suggesting a gradual transformation (obliteration of the lattice structure). At +80° the influence of approaching fusion is apparent. The resistance line does not show any break in this region. Successive runs on the

molten metal gave parallel thermo-electric power lines but with values each time slightly *lower* than the preceding, probably the effect of contamination.

LITHIUM

The lithium was prepared from c.p. lithium chloride by electrolysis of the fused salt. The chloride, obtained from the General Chemical Company and marked c.p., was found on spectroscopic test to contain a trace of sodium, with smaller traces of iron, magnesium and calcium. The metal as obtained by electrolysis showed only the trace of sodium, the other impurities being eliminated in the reduction. The electrolysis was carried on in a nickel crucible with an Acheson graphite anode and an iron wire with a loop in the end for a cathode. The electrodes were separated by a partition of quartz instead of the usual asbestos board which was found to introduce impurities. The melting point was determined as 183.0°C. Values given by Landolt-Börnstein are 180° (Bunsen 1855), 186° (Kahlbaum 1900), and 179° for the freezing point (Zukowsky; Masing and Tammann 1910).

The lithium metal was extruded into the form of a wire through an iron die. A piece about three inches long and 1/16 inch diameter was slipped into a quartz tube which it fitted closely. The constantan and platinum leads were pushed into the metal which was melted for this purpose for a few millimeters at each end by a Bunsen flame. The work on lithium was by far the most satisfactory as regards reproducibility on different runs and with different specimens. The quartz tube containing the metal wire was immersed in "nujol." On melting, capillarity was found to hold the liquid metal in the tube with no other constraint at top or bottom. Readings were thus obtained on thermo-electric power to 285°C, the metal still retaining its silvery luster at that temperature. Earlier readings on the molten metal in lead glass tubes had to be discarded on account of reaction with the glass. In quartz, however, no contamination occurred even at 285°C. Attempts were not made to run the temperature higher. The curves for lithium for both thermo-electric power and resistance, Fig. 8, shows very clearly a transformation at about +50°C.³ There can be no question about the linear relation for thermo-electric power in this case, nor of the presence of α and β forms. The temperature range is sufficiently great to allow of no room for doubt and the closeness with which the points fit the lines on successive runs and with different specimens is quite remarkable. The black points or filled in circles represent data on a second specimen, the readings on which began at about 50°C and continued through change of state to

285°C and then back, the return indicated by the black points with tails. It will be noted that, even after melting and heating to 285° and freezing again, the thermo-electric power line was exactly duplicated except for a lag at the freezing point. The resistance line is perfectly straight from -190°C to +50°C. The deviation of the resistance line above 50°C is very definite. With the first specimen the resistance at 0°C was at first 0.00427, after the low temperature observations the value was 0.00428. A second specimen showed a zero resistance as .00417, and

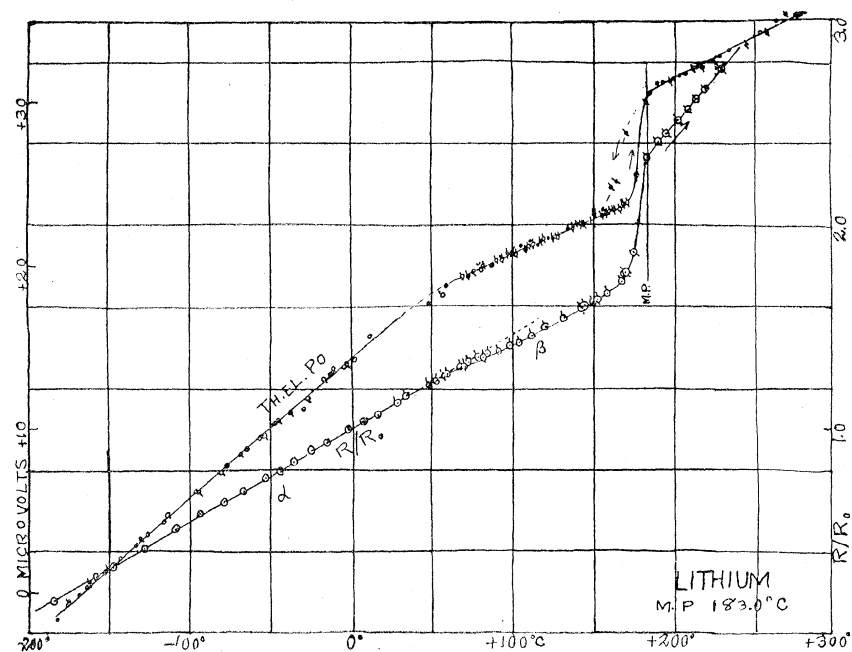


Fig. 8. Curves for lithium, m. p. 183.0°C.

still the same value after heating to +171°C. After fusion and heating to 230°C the resistance had increased to 0.00515. After melting in the tube and freezing again the specimen was found to fit the tube more loosely than originally. As the metal was much lighter than the "nujol" in which it was immersed, the effect of gravity and capillarity was apparently to cause a slight stretching with diminution of cross-section and consequent increased resistance. There was no oxidation or contamination.

GENERAL DISCUSSION

Resistance. A comparison of the temperature coefficients of resistance found in this work with values reported by others should be of interest in view of the existing wide disagreement. Some of the lack of agreement

is probably due to ignorance of the transformations revealed by the present work. Likewise coefficients computed from data taken within 20° or 30° of the melting point would be very high and of little value for purposes of comparison. The values tabulated, Table I, give the coefficients through the ranges indicated. Thus α_{100} means the change in resistance per degree at 100°C divided by the resistance at 100°C.

TABLE I⁴
COMPARISON OF TEMPERATURE COEFFICIENTS AS DETERMINED BY VARIOUS OBSERVERS

	Bidwell	Bridgman	Northrup	Bernini	Hornbeck ⁵
Lithium	0° to 50°C $\alpha_0 = .00457$ 50° to 150°C $\alpha_0 = .00380$ 200° to 300°C $\alpha_{200} = .00366$	0° to 100°C $\alpha_0 = .00458$		0° to 178°C $\alpha_0 = .00431$ 180° to 200°C $\alpha_{200} = .00206$	
Sodium (liquid)	20° to 75°C $\alpha_0 = .00530$ At 100°C $\alpha_{100} = .00425$	20° to 75°C $\alpha_0 = .00552$ At 100°C $\alpha_{100} = .00325$	20° to 93.5°C $\alpha_0 = .00530$ At 100°C $\alpha_{100} = .00330$	0° to 100°C $\alpha_0 = .00428$ At 100°C $\alpha_{100} = .00279$	6° to 88° $\alpha_0 = .00513$
Potassium (liquid)	0° to 50°C $\alpha_0 = .00553$ At 100°C $\alpha_{100} = .00375$	0° to 50°C $\alpha_0 = .00512$ At 95°C $\alpha_{95} = .00403$	0° to 50°C $\alpha_0 = .00580$ At 95°C $\alpha_{95} = .00342$	0° to 50°C $\alpha_0 = .00601$ 90° to 100°C $\alpha_{95} = .00358$	5° to 58° $\alpha_0 = .00552$

A comparison of the coefficients of resistance for the five metals at various temperatures as given by the writer's data is shown in Table II and graphically in Fig. 9. For the liquid metal the values have been corrected for the expansion of glass by assuming the cross-section increased by the fractional amount .00014 (twice the linear coefficient of expansion of lead glass). The coefficients of specific resistance would thus be greater than the observed values by this amount. The consistent decrease in the temperature coefficient of resistance with increasing atomic weight suggests a relation between these quantities.

TABLE II
Temperature Coefficients

	α_{-100}	α_{+100} (liquid)	α_0 (liquid)*
Lithium	.00820	.00599*	.01404
Sodium	.00730	.00440	.00758
Potassium	.00712	.00389	.00604
Rubidium	.00663	.00328	.00470
Caesium	.00638	.00244	.00311

* Extrapolated

⁴ See summary of previous work on the alkali metals at the end of this paper for references and comments.

⁵ Hornbeck, Phys. Rev. **2**, 217 (1913).

The coefficient for liquid rubidium is too high to fit the smooth curve upon which the other values lie. It should be noted that this value was obtained on the impure specimen, which melted at 33.0°C, the coefficient not being obtained for the purer specimen which melted at 37.2°C. This probably accounts for the discrepancy.

Thermo-electric power. Fig. 10 shows the thermo-electric power lines plotted to the same scale. The curves so plotted bring out interesting similarities in the thermo-electric behavior of sodium and potassium and

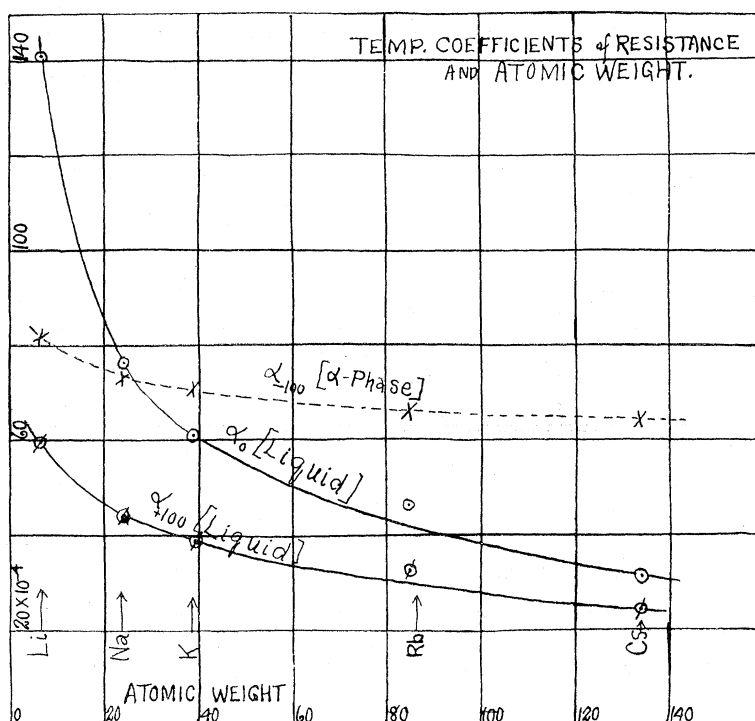


Fig. 9. Temperature coefficients of resistance as a function of atomic weight of alkali metal.

of rubidium and caesium. The lines for liquid sodium and potassium have very nearly the same slope. The same is true for the lines for liquid caesium and rubidium. Also the sodium and potassium lines have the same slope in the β form. The lead to platinum line is shown dotted, the line being taken for soft platinum from the paper of Tait.⁶

It is believed that the change in thermo-electric power at the melting point, as brought out by these curves, has never been clearly shown before. Richardson⁷ says "we should expect these changes in electrical

⁶ Tait, Trans. Roy. Soc. Edin., p. 125, 1873

⁷ Richardson, The Electron Theory of Matter, p. 463

conductivity (on melting) to be accompanied by very considerable changes in the Peltier effect and in the thermo-electric power. Such effects have been looked for most carefully and with negative results."

The sign of the thermal e.m.f. was determined in all cases according to the usual convention, viz., if current flows across the hot junction from the metal being investigated to platinum, the metal is then said to be negative to platinum, i.e., regarding the junction as a source of e.m.f. the current then flows in the external circuit from platinum to the metal.

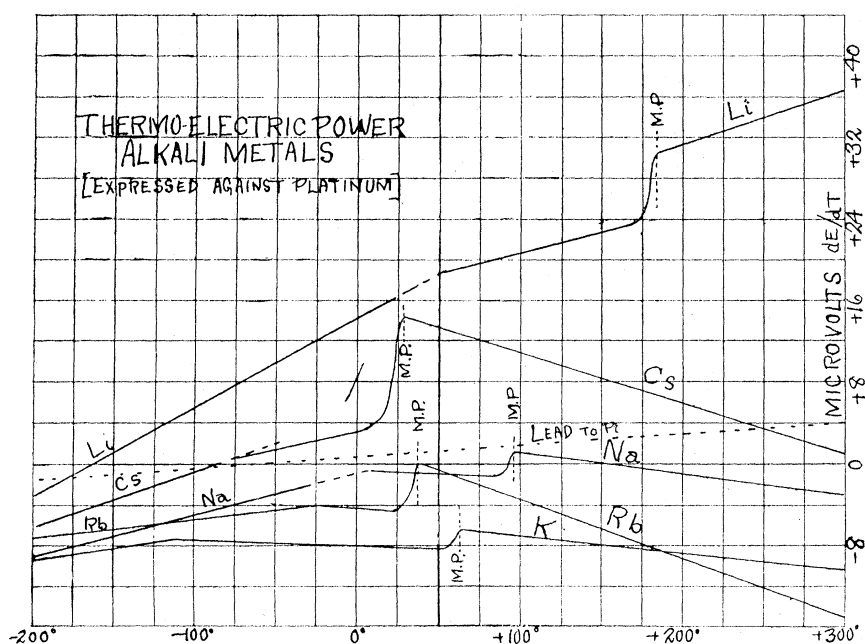


Fig. 10. Thermo-electric power of alkali metals against platinum.

THE SPECIFIC HEAT OF ELECTRICITY

As originally shown by Lord Kelvin we may compute from thermo-electric data the so-called specific heat of electricity. It has been suggested by G. K. Lewis⁸ that the excess atomic heat above the equipartition value, in the cases where that value is exceeded, is due to the acquisition of energy by the electrons, or the excess is the atomic heat of the electrons. Likewise Lewis has shown⁹ that the electrons, even though their number equals that of the atoms, should not themselves have the equipartition value, that value being departed from because of the small mass and the constraints under which the electrons are held.

⁸ Lewis, Proc. Nat. Acad. Sci. 4, 25 (1918)

⁹ Lewis, Phys. Rev. 4, 331 (1914)

The expression for specific heat of electricity is obtained in the following way. From the First Law of Thermodynamics, assuming one of the metals of the couple to be lead,

$$dE = d\pi + \sigma dT \quad \text{or} \quad dE/dT = d\pi/dT + \sigma$$

where dE/dT is the thermo-electric power; π , the Peltier e.m.f.; σ , the Thomson e.m.f. per degree difference along the material. σ is the energy absorbed in carrying unit mass of electrons from a given point in the metal to a point one degree higher in temperature.

By application of the Second Law we have also

$$dE/dT = \pi/T \quad \text{or} \quad \pi = T dE/dT,$$

which when differentiated and combined with the above gives

$$\sigma = -T d^2E/dT^2.$$

The quantity d^2E/dT^2 may be obtained from the curves (Fig. 10) expressed in micro-volts per degree, per degree. When multiplied by T and by the factor .023074¹⁰ we have σ in calories per degree per gram equivalent. The gram equivalent refers to the atomic weight in grams of the metal in question on the assumption that there is one electron available from each atom to share in the specific heat. A comparison of values of σ obtained from thermo-electric data with values computed from the excess in atomic heat has been made by Latimer¹⁰ for a large number of elements. The more extensive data on the alkali metals afforded by the present work justify further comparison of the atomic heat of the electrons as computed in these different ways. Table III column (1) shows the slopes of the thermo-electric power lines, expressed in microvolts per degree per degree, and corrected to lead. Columns

TABLE III
Specific Heat of Electrons

	d^2E/dT^2			σ in calories		Observed excess of C_p over 6.4
	α	β	liquid	β (solid) At 20°C	liquid At 100°C	
Lithium	+.075	+.032	+.040	-0.216	-0.348	{ -0.53 at +20°C +0.88 at +100°C +0.39 at +20°C +0.70 at +14°C
Sodium	+.032	+.025	-.0282	+0.16	+0.24	
Potassium	+.009	-.0205	-.0275	+0.14	+0.23	
Rubidium	+.007	-.0205	-.069		+0.59	
Caesium	+.040	+.022	-.062		+0.53	

(2) and (3) show σ computed from these slopes. It is worthy of note that the values for sodium and potassium are nearly alike, as are also those of caesium and rubidium. There seem to be no data on the specific heats of the alkali metals in the liquid state although considerable

¹⁰ Latimer, Am. Chem. Soc. Jour. **44**, 2136 (1922)

data for extreme low temperatures are available. Eastman and Rodebush¹¹ give for the atomic heat of sodium at 20°C (their highest value) $\alpha C_p = 6.79$, $\alpha C_v = 6.29$, and for potassium at +14°C, $\alpha C_p = 7.10$ and $\alpha C_v = 6.52$. The atomic heat of lithium αC_p , according to Laemmel¹² has the following values; at 0°C, 5.56; at 50°C, 6.33; at 100°C, 7.28; at 190°C, 9.61. The thermo-electric data give the atomic heat at constant pressure. The average value of the atomic heat of the elements at constant pressure is 6.4. The excess above this rather than the excess over the equipartition value of 5.97 should probably be taken as giving the atomic heat of electrons. The excesses so computed from the available experimental data are given in column (4). Lindemann¹³ computes 0.266 cal. as the atomic heat of the electrons at 27°C, a computation based on Debye's formula for specific heat, assuming the compressibility of the "electron space lattice" equal to that of silver. It is significant that the specific heat of electrons in the β form of lithium, sodium and potassium is nearly the same as in the liquid form; also that in the α form, the low temperature modification, the specific heat of the electron is negative in all cases. A negative σ is not unusual. It occurs in iron, nickel, platinum and other metals. The comparison afforded in Table III indicates that the heat capacity of the electrons as determined from thermo-electric data, assuming that we may properly interpret σ in this way, accounts for only a portion of the excess above the equipartition value. The fact that σ is sometimes negative needs interpretation.

A study of the crystal structure of the alkali metals at various temperatures is being undertaken with the hope of getting direct proof that the breaks in the thermo-electric power lines are due to crystalline modification as here assumed.³

CORNELL UNIVERSITY,
August, 1923.

Previous work on the alkali metals. The most extended observations on the temperature-resistance relations of the alkali metals are to be found in the papers of Bernini,¹⁴ Northrup¹⁵ and Bridgman;¹⁶ and on thermo-electric properties in the work of Bernini,¹⁷ Broniewski and Hackspill¹⁸ and Barker.¹⁹ For the resistance of caesium

¹¹ Eastman and Rodebush, *Jour. Am. Chem. Soc.* **40**, 498 (1918)

¹² Laemmel, *Ann. der Phys.* (4) **16**, (1905)

¹³ Lindemann, *Phil. Mag.* (6) **29**, 135 (1915)

¹⁴ Bernini, *Phys. Zeits.* 1904, pp. 241, 406; 1905, p. 74

¹⁵ Northrup, *Trans. Am. Elec. Chem. Soc.* **20**, 185-204, 1911; *Jour. Franklin Inst.* **175**, 153-161, 1913

¹⁶ Bridgman, *Proc. Am. Acad. Arts. and Sci.* 56-3, Feb. 1921

¹⁷ Bernini, *Nuovo Cimento*, **15**, 29-42, 1908

¹⁸ Broniewski and Hackspill, *C. R.* **153**, 814, 1911

¹⁹ Barker, *Am. Jour. Science* (4) **24**, 159, 1907

and rubidium we have only the pioneer work of Hackspill,⁷ Broniewski and Hackspill,²⁰ and Guntz and Broniewski.²¹ The earliest work on the alkali metals is that of Matthiessen,²² who made measurements on the resistance of sodium and potassium both on extruded wires and on specimens contained in capillary tubes. The measurements covered the range from 0° to 80° for potassium, and from 0° to 120° for sodium. He shows the large increase in resistance which occurs on change of state. His potassium melted between 46.8° and 56°, and therefore was not of high purity. His sodium was better, as its melting point was between 95.4° and 96.1°. The measurements of Bernini were more extensive. They were made on metals in capillary glass tubes immersed in oil. The observations for sodium and potassium were made through the range 0° to 130°, and for lithium through the range of 0° to 233°. Bernini's data do not agree with the observations of others, as indicated by the temperature coefficients, which have been tabulated for purposes of comparison, (Table I). His lithium melting point was 178°, indicating considerable impurity. His sodium melting point was good, yet his temperature coefficient (0°–100° range) is about 40 per cent lower than the values of others. He does not show sufficient data above the melting point to warrant a computation of the temperature coefficient of liquid sodium. His potassium melting point is about half a degree low, and the temperature coefficient (0° to 50° range) is considerably higher than that observed by others. Bridgman's measurements on solid lithium were made at four temperatures only, 0°, 25°, 50°, 75°, straddling a transformation region as indicated by the writer's data. His observations on molten lithium were made on an impure sample contained in a metallic capillary. On liquid potassium Bridgman made observations at three temperatures only. Bridgman's sodium melting point was 97.62°, indicating possibly better purity than my sample, which melted at 97.0°. The resistance data on caesium and rubidium are very meager consisting of a few observations between 0° and 40°, and at –78° and –183°. Low temperature readings on lithium, sodium and potassium likewise are recorded only for these two easily obtainable temperatures.

²⁰ Hackspill, C. R. **151**, 305, 1910

²¹ Guntz and Broniewski, C. R. **147**, 1478, 1908

²² Matthiessen, Phil. Mag. (4), **12**, 199, 1856; (4) **13**, 81, 1857