THERMAL AND ELECTRICAL CONDUCTIVITIES OF THE ALKALI METALS.

By J. W. Hornbeck.

I. Introduction.

ONE of the first successes of the modern electron theory consisted in its very simple explanation of the constant ratio of the thermal and electrical conductivities for the metallic elements. However, a closer study of the conduction of heat and electricity through metals, of their thermo-electric and magnetic properties, showed that the simple theory, which considered the electrons to move freely through the metal, was unable to explain the manifold and complicated phenomena in a satisfactory way.

It was first assumed, in the theories of Riecke, Drude, J. J. Thomson and H. A. Lorentz, that the electrons are free and share the heat motion of the atoms; but this assumption leads to a number of contradictions. When one determines N, the number of free electrons per cubic centimeter, by the method of the conductivities for heat and electricity for the different metals, values are found which differ greatly[1] from those derived from the Peltier effect. Moreover, the experiments of Rubens and Hagen show that the electrical conductivity of metals for alternating currents of very high frequency remains practically the same as for steady forces, and the values of N which follow from these data are impossible[1] in view of the known values of the specific heat. Furthermore, Lees[2] measured the thermal and electrical conductivities of a number of metals down to the temperature of liquid air and found an increasing deviation from the law

$$\frac{\lambda}{\sigma} = \frac{4}{3}\frac{\alpha^2}{e^2}T.$$

A change in structure has a large effect on the thermal and electrical conductivities. For instance it has been found recently[3] that the resistance of mercury at 4.2° absolute drops suddenly from 0.11 to zero. Small impurities have large effects. Metals and alloys often behave in opposite ways. For example, the heat conductivity of the metals de-

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[1] J. J. Thomson, Corpuscular Theory of Matter, pp. 76, 84.

[2] C. H. Lees, Phil. Tran., Royal Soc., Vol. 208, p. 381, 1908.

[3] H. Kamerlingh Onnes, Com. Phys. Lab. of Univ. of Leiden, No. 124, p. 23.

creases slightly with increasing temperature, while for the alloys it increases with the temperature. Moreover, the ratio $\lambda/\sigma T$ increases slightly between $-180°$ C. and $+20°$ C. for the metals, and decreases considerably for the alloys.

These facts cannot be explained by the present theories even when it is assumed, as Lorentz and Richardson[1] have done, that the distribution of the velocities of the electrons is that which corresponds to Maxwell's expression.

The strongest evidence against this conception of the electric current consists in the fact, shown by Nernst, that the specific heat of metals approaches zero as the temperature approaches the absolute zero. If the current were due to the motion of free electrons which are in temperature equilibrium with the metal, then the specific heat would be due mainly to the free electrons and would therefore, as in a gas, change very little with decreasing temperature. The question arises as to whether the electrons carrying the current take part in the specific heat.

Several modifications of the original theory have been proposed, but none of them gives an adequate quantitative explanation of all the phenomena. The various theories agree only in the fundamental assumption that the current is carried by electrons. This is in harmony with the general facts that the good conductors are metals, positive elements, ready to part with a negative electron; that the metals when struck by ultra-violet light or Roentgen rays, or when heated to a certain temperature, emit electrons; and that the current in the metals shows the Hall effect.

The decrease of the specific heat with decreasing temperature is at least qualitatively accounted for by Planck's theory of radiation. It is possible that the electrons have at low temperature no part in the specific heat of the metals, so that the specific heat is entirely due to the motion of the atoms or to their elementary oscillators. According to this conception there are no free electrons at all, at least at low temperatures, and the electrons escape only when they have acquired a sufficient amount of kinetic energy to overcome the attraction of the positive "rest-atom." Then there should be a definite relation between the energy of the electron and the energy of the atom.

We shall assume that the electrons part with the atom when their kinetic energy is proportional to the energy E of the atom. Moreover, for the energy of the atom, or the oscillator in the atom, we shall assume the expression given by Planck[2]

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[1] Planck, Acht Vorlesungen über Theoretische Physik.

[2] O. W. Richardson, Trans. Am. Chem. Soc., Vol. XXI., 1912.

$$E = \frac{hn}{e^{\frac{hn}{kT}} - 1},$$

or, according to the modified theory,

$$E = \frac{hn}{e^{\frac{hn}{kT}} - 1} + \frac{hn}{2}.$$

Then the kinetic energy of the electron is given by

$$E_1 = \tfrac{1}{2}mv^2 = \gamma \frac{hn}{e^{\frac{hn}{kT}} - 1},$$

where γ is some constant, and from this equation we know v as a function of T. The constant term $hn/2$ has no effect in the present application of the Planck theory. If l is the mean free path and t the time during which the electron moves from one atom to the other, then

$$v = \frac{l}{t}.$$

The force acting on the electron in the field E' is $E'e$, and the acceleration

$$a = \frac{E'e}{m}.$$

The mean time during which this force acts is $t/2$ seconds and hence the field superposes a velocity

$$u = \frac{at}{2} = \frac{E'el}{2mv}.$$

The number of electrons passing through unit cross-section per unit time is

$$Nu = \frac{NE'el}{2mv},$$

and the current density

$$i = Nue = \frac{E'e^2Nlv}{2mv^2} = \sigma E'.$$

Whence

$$\sigma = \frac{e^2Nlv}{2mv^2} = \frac{Nlve^2}{4E_1} = \frac{Nlve^2.}{4\gamma \frac{hn}{e^{\frac{hn}{kT}} - 1}}. \qquad (1)$$

For the quantity of heat energy passing through unit area per unit time, we have

$$H = \frac{1}{3} Nvl \frac{\partial E_1}{\partial x} = \frac{1}{3} Nvl \frac{dE_1}{dT} \frac{dT}{dx} = \lambda \frac{dT}{dx}.$$

And

$$\lambda = \frac{1}{3} Nvl \frac{dE_1}{dT}. \qquad (2)$$

Hence

$$\frac{\lambda}{\sigma} = \frac{4}{3e^2} \frac{dE_1}{dT} E_1. \qquad (3)$$

Substituting in (3) the values of E_1 and dE_1/dT, we have

$$\frac{\lambda}{\sigma T} = \frac{4}{3} \frac{\gamma^2 h^3 n^3}{e^2 k} \frac{1}{T^3} \frac{e^{\frac{hn}{kT}}}{\left(e^{\frac{hn}{kT}} - 1\right)^3}. \qquad (4)$$

If hn/kT is small, we can expand the exponential functions and equation (4) for the higher temperatures assumes the form

$$\frac{\lambda}{\sigma T} = \frac{4}{3} \gamma^2 \frac{k^2}{e^2} \left(1 - \frac{hn}{2kT}\right). \qquad (5)$$

As T increases, according to equation (5), the values of $\lambda/\sigma T$ should approach a constant value and this agrees with the facts. Moreover, when the values of $\lambda/\sigma T$ are plotted against T in equation (4), the curve is found to be of the same form as the experimental curves which Lees obtained for the pure metals at low temperatures. Thus we have a formula which explains the behavior of $\lambda/\sigma T$ for pure metals and which also leads approximately to the right expression for the variation of the specific heat with the temperature. It agrees with Einstein's formula for specific heat; in fact, both formulæ rest upon Planck's expression for E.

It is not claimed that this theory is complete. It is merely suggested as a possible step in the right direction because it removes two important difficulties of the electron theory without introducing new contradictions. The phenomena of metallic conduction are so complicated that they cannot be explained by one simple group of assumptions. So far we have considered only the heat conductivity due to the electrons. The atoms themselves undoubtedly transfer a part of the heat motion as is shown by the fact that non-conductors of electricity have finite values of λ while σ is equal to zero. Moreover, there are good reasons for believing l, the mean free path, is a function of the temperature. This would follow from Richard's theory in regard to the variation of the radius of the atom. It should be pointed out that if we take the two most simple formulas

$$\lambda = \frac{1}{3} Nlv\alpha,$$

$$\sigma = \frac{Nle^2}{2mv},$$

and assume $\frac{1}{2}mv^2 = \alpha T$ and also $l = \mathrm{const} / \sqrt{T}$, it follows that λ becomes independent of the temperature, while σ is inversely proportional to the absolute temperature. This agrees fairly well with experimental facts over a considerable range of temperature. That the mean free path has something to do with the conductivity is also shown by the Hall effect. H. Kamerlingh Onnes has found that the constant of the Hall effect for gold, silver and mercury, increases considerably near the temperature of liquid hydrogen.

Finally, the electric field may act on the atoms in a metal, tending to bring about a certain polarization which will have an effect on the conductivity for electricity and heat. If this were the case, we should expect the use of temperature baths to lead to a value of λ different from that obtained by electric heating.

It was the purpose of the present investigation to attempt to bring further evidence in favor of one of the different theories. The alkali metals were thought to be particularly suited to this purpose because they have properties quite different from those of the other metals. Alkali metals have a higher temperature coefficient of resistance than the other metals. The atomic heat and atomic volume are greater and the index of refraction smaller than for the ordinary metals. In their photoelectric properties they differ considerably from the other elements. All these properties indicate that the alkali metals are rich in electrons and that even the positive "rest-atoms" have considerable mobility.

So far as known, the heat conductivity of the alkali metals has hitherto not been measured. This is a constant of sufficient importance to make its determination worth while. Northrup[1] has determined the electrical conductivity of the alkali metals by a very good method and claims an accuracy of one half of one per cent. His results, however, do not agree well with those of former observers[2] and it was therefore considered important to check his work by an entirely different method.

II. Theory of the Method.

The original Kohlrausch[3] method, which was perfected by Jaeger and

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[1] E. F. Northrup, Trans. Am. Electro-Chem. Soc., Vol. XX., 1911, p. 185.

[2] Mattheisen, Phil. Mag. (4), 12, 199, 1856; 13, 81, 1857. Bernini, Phys. Zeit., 5, 241, 1904.

[3] F. Kohlrausch, Gött. Nachr., S. 83, 1874; Pogg. Ann., 156, S. 616, 1875; Ann. der Phys., (4) I., 145, 1900.

Diesselhorst,[1] was used. It is both simple and reliable and it has the distinct advantage of giving the ratio of the heat and electrical conductivities directly. This method consists, briefly, in sending a steady electric current through a cylindrical rod of the metal to be investigated and measuring the temperature and potential difference at three equidistant points along the axis of the rod, while the temperatures of the ends of the rod and of the surrounding jacket are held constant. For the convenience of the reader the theory of the method, so far as it has any application to this investigation, will be given here in a simplified form.

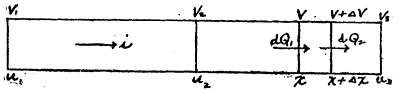

Fig. 1.

Referring to Fig. 1, let u and v represent the temperature and potential of any cross-section of the rod; and let

a = area of cross-section,
σ = electrical conductivity,
λ = thermal conductivity.

Let us assume that the Thomson effect is negligible and that λ and σ, for the small temperature interval considered, are constant. Then the current flowing through the rod is given by

$$i = \left(-\frac{dv}{dx}\right)\sigma a.$$

And the number of calories of heat developed in the elementary volume per unit time is

$$dQ = \frac{i^2}{\sigma} \cdot \frac{dx}{a} \cdot \frac{1}{J},$$

where J represents Joule's equivalent,

$$dQ = \left(\frac{dv}{dx}\right)^2 \sigma a \frac{dx}{J}.$$

The quantity of heat flowing into the elementary volume per unit time is

$$dQ_1 = \left(-\frac{du}{dx}\right)\lambda a,$$

and the quantity flowing out is, likewise, equal to

$$dQ_2 = -\frac{du}{dx}\lambda a - \frac{d^2u}{dx^2}\lambda a dx.$$

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[1] Jaeger und Diesselhorst, Wiss. Abh. der Phys. Tech. Reich., 3, 269, 1890; Sitz. Ber. Der Berlin Ak. d.w., 38, 719, 1899.

For the stationary state

$$dQ + dQ_1 - dQ_2 = 0. \qquad (1)$$

Substituting in this equation, we have

$$\left(\frac{dv}{dx}\right)^2 \frac{\sigma}{J} + \frac{d^2u}{dx^2}\lambda = 0. \qquad (2)$$

Now the isothermal surfaces are also equipotential surfaces, if we assume that the temperature is constant for all points of the same cross-section, and the temperature depends upon the potential only. Then

$$\frac{du}{dx} = \frac{du}{dv}\frac{dv}{dx}.$$

And

$$\frac{d^2u}{dx^2} = \frac{d^2u}{dv^2}\left(\frac{dv}{dx}\right)^2 + \frac{du}{dv}\frac{d^2v}{dx^2}.$$

But

$$\frac{d^2v}{dx^2} = 0,$$

$$\frac{d^2u}{dx^2} = \frac{d^2u}{dv^2}\left(\frac{dv}{dx}\right)^2.$$

Substituting this value in equation (2), we have

$$\left(\frac{dv}{dx}\right)^2 \frac{\sigma}{J} + \lambda\frac{d^2u}{dv^2}\left(\frac{dv}{dx}\right)^2 = 0.$$

Or

$$\frac{d^2u}{dv^2} = -\frac{\sigma}{J\lambda}. \qquad (3)$$

Integrating this equation, we have

$$\frac{\lambda J}{\sigma}u = -\frac{v^2}{2} + Av + B. \qquad (4)$$

The integration constants, A and B, are readily evaluated by imposing the condition

$$u_1 = u_3 = u',$$

and the equation can be reduced to the form

$$\frac{\lambda}{\sigma} = \frac{1}{8}\cdot\frac{1}{J}\cdot\frac{(v_1 - v_3)^2}{u_2 - u'}, \qquad (5)$$

where u_2 is the temperature of the middle of the rod, and u' is the temperature of either of the two sections equally distant from the middle.

Equation (5) would be true if no heat were lost through the lateral surface of the rod. This condition, however, cannot be realized experimentally and so it is necessary to apply a correction.

Let us change (5) slightly by expressing λ in watt-seconds, instead of calories, and put

$$V = \tfrac{1}{2}(v_1 - v_3),$$

$$U = u_2 - u' = u_2 - \tfrac{1}{2}(u_1 + u_3).$$

Then we have

$$\frac{\lambda}{\sigma} = \frac{V^2}{2U}. \tag{6}$$

In this equation, then, U stands for the value of the temperature difference, supposing that the surface of the rod were covered with a perfect heat insulator.

Now let Δ represent the observed value of the temperature interval $u_2 - \tfrac{1}{2}(u_1 + u_3)$; let u_0 represent the temperature of the surrounding jacket; and let

$$N = u_0 - u_2 + \tfrac{1}{6}\Delta.$$

Then, as Jaeger and Diesselhorst have shown,[1]

$$U = \Delta - \epsilon N, \tag{7}$$

where ϵ is a correction factor depending on the conductivity of the packing, the conductivity of the metal, and the dimensions of the rod experimented upon; and its value can be determined by experiment.

In the present work with the alkali metals, the values of λ/σ were computed by means of equations (6) and (7).

$$\epsilon = \frac{\Delta}{N},$$

for the case where no heating current is used. The method of obtaining this correction factor will be made clear in a later chapter.

III. APPARATUS.

End Baths.—The apparatus for controlling temperatures was constructed in the department shop. It was modeled after that of Jaeger and Diesselhorst, but certain modifications were necessary in order to protect the glass vacuum tubes which contained the alkali metals. The end baths were provided each with a flat brass lid and a rotary stirrer, as shown in Fig. 2, which was driven by a small motor. Fig. 3 indicates the method used to attach the glass tubes to the end baths. In a way

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[1] Wiss. Abh. der Phys. Tech. Reich., 3, 285, 1900.

to be described in detail later, the metal to be studied was poured into glass tubes one or two centimeters in diameter and 30 cm. long. The ends of the tube were closed by copper discs, 2 mm. thick and 5½ cm. in diameter. By means of suitable brass rings, each provided with six screws, the end-discs were attached to annular diaphragms which, in turn, were mounted against the end baths in a similar way so that the alkali metal and the water were separated only by the thin discs of copper. The soft-rubber diaphragms served as a protection for the glass tubes against mechanical strains.

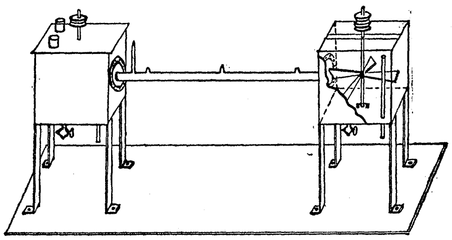

Fig. 2.

The heating-current terminals were introduced beneath the heads of three of the screws symmetrically placed with respect to the center of the discs.

Brass Jacket.—The temperature of the atmosphere of the tubes was controlled by pumping water from a reservoir through a cylindrical brass jacket by means of a small turbine. This jacket was made in two independent parts which were connected at A and B (Fig. 4), and similarly on the opposite side, by short rubber tubes, thus making it necessary for the water to flow the entire length of both semi-cylinders before leaving the jacket. The wires of the thermo-couples were introduced between the two parts of the jacket and were insulated from the brass by thin strips of mica.

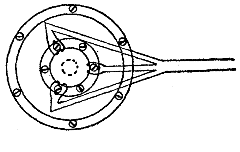

Fig. 3.

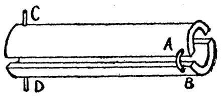

Fig. 4.

The temperature, u_0, of the jacket was measured by two Beckmann thermometers, mounted deep within vertical glass tubes through which the water flowed, so that no stem corrections were necessary. Moreover, these thermometers were placed so that their bulbs were at exactly equal distances from the points C and D respectively. The tubes leading from the jacket to the thermometers were made as short as possible and were packed each with the same number of layers of asbestos paper. Likewise, the glass tubes containing the thermometers were packed similarly so that, even though the two indicated temperatures which differed considerably when working far from room-temperature, still the arithmetic mean of the two readings gave the true mean temperature of the water in the jacket.

The space surrounding the tube within the brass jacket was packed tight with cotton wool and the outside surface of the jacket was wrapped with fourteen layers of heavy cotton flannel.

Galvanometer.—The galvanometer used was of the D'Arsonval type and designed especially for work with thermo-couples. It has a resistance of 230 ohms, a period of four seconds, and a sensibility of 210 megohms for a scale distance of 1 meter. By means of an unusually good lens, however, the image of a lamp filament was brought to a sharp focus on a scale 5½ meters distant from the mirror. At 5½ meters the sensibility was 8.6×10^{-10} amperes per millimeter deflection. The E.M.F. of the copper-constantan thermo-couples was about 40 microvolts per degree, giving deflection of 0.2 mm. per 1/1000 degree. Thus a change in temperature of one thousandth of a degree could be detected.

Ammeters and other Apparatus.—Except for the potassium tube, where the value of the heating current sometimes exceeded 150 amperes, a new Siemens and Halske ammeter was used. It was standardized by means of a Wolff potentiometer, Weston standard cell, and a standard 0.01 ohm resistance. For the data on potassium a Weston direct reading ammeter (0–200) was used. This was put in series with the new ammeter, mentioned above, and calibrated for the range over which it was used.

All of the standard thermometers except No. 17,481 were standardized at the Reichsanstalt. No. 17,481 was certified by the Bureau of Standards. These thermometers were graduated to tenths of a degree.

An Otto Wolff potentiometer, Otto Wolff resistance boxes, and a Weston standard cell were used.

The heating current was supplied by the department storage battery.

Arrangement of the Electrical Apparatus.—The potentiometer, P, was connected as shown in Fig. 5. B_1 was a small storage cell; B_2, the standard cell; R_1, R_2 and R_3 were resistance boxes. By adjusting R_3 at the beginning of a run, the potential difference from A to C was made equal to the E.M.F. of the standard cell. R_1 and R_2 were kept constant.

The switches and keys of the potentiometer circuit which had to be operated continually while taking readings, were grouped together on one switchboard shown diagrammatically in Fig. 6. C_1 and C_2 represent commutators of the rocker type; S_1, S_2 and S_3 were two-way switches of the rocker type; K_2 and K_3 were ordinary mercury keys. Six blocks of paraffine were mounted upon a glass plate, 30 × 40 cm., in the positions indicated. The thirty-two mercury wells which were sunk in the paraffine, were all lined by small glass cups which served as supports for the metal rockers. These rockers were all made of copper and only copper wires dipped into the mercury cups, all being wound from the same spool. In this way, contact potential differences were reduced to a minimum.

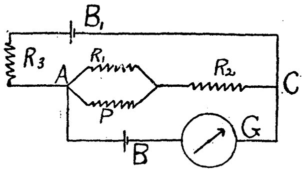

Fig. 5.

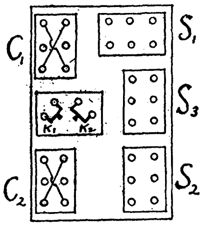

Fig. 6.

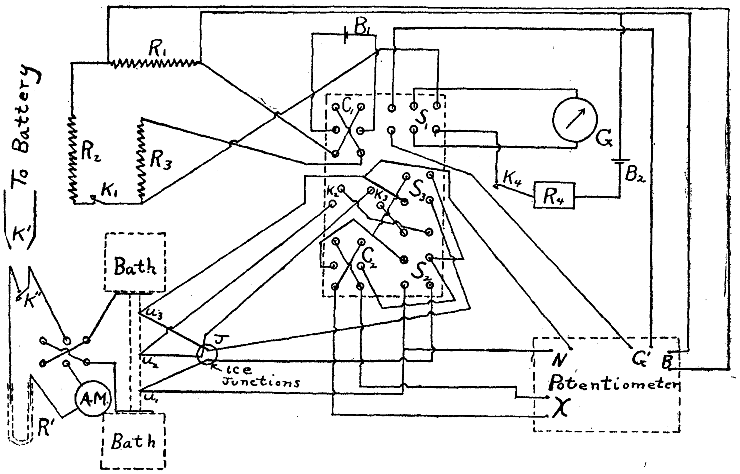

Fig. 7.

Fig. 7 shows a diagram of the exact connections of the electric circuits and the relative positions of the apparatus, with the exception of the galvanometer which was on a wall bench on the opposite side of the room, 5½ meters away. The ammeter, A.M., commutator C', controlling resistance R', and key K'', were all within easy reach of the observer. K'' was a short-circuiting key to avoid arcing when the rocker of C' was thrown over. R_4 was simply a protective resistance for the galvanometer and standard cell, and could be cut out of the circuit by a suitable plug.

IV. EXPERIMENTAL DETAILS.

Construction of Thermo-couples.—Since the alkali metals dissolve ordinary solder, it could not be used for the junctions which were placed in the tubes. Moreover, it was not an easy matter to hard-solder the junctions without burning the minute copper wires. Several attempts to do this having failed, it was decided to try the use of mechanical contacts. The fine copper wire, 0.12 mm. in diameter, was wound around the constantan wire (diam. 0.18 mm.) for a distance of about 2 mm. The shape of these junctions was admirably adapted to the double purpose of measuring both the temperature and potential difference between two cross-sections. They were mounted in a tube of sodium-potassium alloy but the data was inconsistent and on removing the junctions from the tube and attempting to check their calibration, it was found that two of the three calibration curves had shifted by an amount equivalent to more than one tenth of a degree.

So it was considered necessary to solder the wires together. The method which finally succeeded was as follows. Nearly equal weights of copper and silver were melted together with a small blast flame. A junction formed by two or three turns of the copper wire around the constantan, was moistened and covered with powdered borax. Then, at a time when the temperature of the silver-copper alloy was just above the melting point, the junction was dipped beneath the surface of the globule and quickly removed.

Junctions could be soldered in this way without any injury to the delicate wires. Such junctions, therefore, were used in the last three tubes experimented upon,—the three for which the data are given in this paper. The ice junctions were soldered with ordinary soft-solder.

For the alloy tube and the potassium tube, copper wire 0.12 mm. in diameter was used. However, it was found to be almost impossible to go through the long process of calibrating the thermo-couples, mounting them into the tube, filling the tube, and finally mounting the tube between the water-baths, without breaking one of these frail wires at some point where it could not be soldered,—thus involving the loss of the thermo-couple and several days' work. Consequently, somewhat larger copper wires were used in the sodium tube. In this case the diameter of the wire was 0.16 mm. It can be shown, however, that the error due to the conductivity of this wire was negligible for the conditions under which it was used. For all three of the tubes the constantan wire used had a diameter of 0.18 mm.

Platinum-constantan thermo-couples were used in the lead rod because, at that time, it was thought platinum wire would be used in the case of the alkali metals since it could be sealed into the glass, but the plan proved impracticable.

Calibration of the Thermo-couples.—The thermo-junctions and thermometer were mounted within a large Dewar flask which contained also a rotary stirrer. For the lower temperatures salt and ice were used to keep the temperature from rising, while for the higher temperatures steam was introduced slowly through a small tube near the wall of the flask at a point diametrically opposite the position of the thermo-junctions and thermometer. The temperature in this way could be held very steady by regulating the gas pressure of the three Bunsen flames which heated the boiler. The rotary stirrer was run by a small motor.

For the first few calibration curves a cathetometer was used to read the thermometer scale. This, of course, was a most accurate method, but it involved the difficulty of holding the temperatures constant for several minutes at a time, since the vernier had to be adjusted and read both before and after balancing the potentiometer for direct and reversed currents. Consequently, it was decided to try a direct-reading eye-piece attached to the stem of the thermometer. By this method the data for a point on the calibration curve could be obtained so much more quickly that the loss in accuracy of the scale reading was almost compensated by the gain in time and consequent smaller variation in the temperature. Readings were taken at intervals of about one or two tenths of a degree over the particular range where the curves were to be used and, when the points were plotted, there was no doubt about the proper position of the line.

The curves obtained in this way were reliable to about three or four thousandths of a degree, for the measurement of temperature differences; and, since this was as high a degree of accuracy as was required in the calibration, the use of the cathetometer was abandoned in favor of the quicker and less laborious procedure.

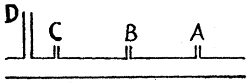

Fig. 8.

Preparation of the Tubes.—The kind of tube used to contain the alkali metals is shown in Fig. 8. The side tubes *A*, *B* and *C*, through which the thermo-junctions were introduced, were about 2 mm. in diameter and 10 cm. apart. They were sealed on in such a way as to change the cross section of the main tube as little as possible. The filling tube *D* was always placed at least 4 cm. from *C*. The diameters of the tubes are given in the data tables. The entire length in each case was about 30 cm.

Considerable difficulty was met in devising a method of sealing in the thermo-junctions so that a vacuum could be maintained at temperatures above the melting point of sealing wax. It was finally accomplished in the following way. The two wires of the junctions, one of which in each case was contained in a minute, slightly funnel-shaped glass tube for insulation purposes, were first sealed into the tube by means of "Quixo Caementium." This is a mineral cement, a commercial article, which was purchased from one of the local dealers. It dries very hard but it is somewhat porous and will hold a vacuum only a short time. Consequently, after the caementium had dried it was covered over with a layer of sealing wax. A kind called De Khotinsky cement was used because it has a higher melting point than the red, "Bank of England" wax. The caementium held the thermo-junctions rigidly in their positions and when the tube was heated the air pressure could not force the soft wax into the tube.

After grinding the ends of the tube they were fitted into circular grooves in the copper end-disks, about 1.5 mm. deep. These joints were filled with litharge (PbO) mixed in boiled linseed oil, and baked for several hours at a temperature of about 100° C. When thoroughly dry and solid they were covered with a thick layer of the Khotinsky sealing wax. The reason for using litharge in place of caementium, for sealing on the end discs, was the fact that it does not dissolve in water,—thus reducing the fire-risk in case of accident.

Before the end discs were sealed on, an accurate scale was introduced within the tube and the thermo-junctions bent into positions which spaced them exactly 10 cm. apart. They extended about 3 mm. into the tube.

The sodium and potassium tubes were prepared as described above. Sealing wax alone, however, was used in the case of the sodium-potassium alloy and for this reason no data could be taken with this tube for temperatures above 45°.

Filling the Tubes.—The method of filling the tubes is illustrated in Fig. 9. The sodium or potassium was introduced into the bulb *D* through an opening at *G*. The tube was then sealed at *G* and the Gaede pump started. After melting the metal, it was kept hot for an hour or more during the exhaustion, in order to drive off all traces of the oil. When the crust finally appeared dry and black, and the discharge tube *F* showed only the presence of the alkali vapor, the system was sealed off at *E*.

Then, holding AB in a horizontal position and keeping it hot with Bunsen flames, the tube D was tilted and the bright, pure metal poured through a system of small funnels at C which held back all of the dross.

It was a very difficult matter to fill a tube because of the formation of bubbles due to vapor pressure, and further, because of the contraction of the metal on cooling. The only way it could be done at all was to pour in metal a little at a time and allow it to solidify before adding any more. Thus it was necessary to melt the successive portions together to avoid layers and this local heating often involved the loss of a tube, either by breaking the glass or by letting the air in through the softened cement at one of the thermo-junctions. When filled, the tube AB was sealed off at a stricture H and it was then ready to be mounted between the water-baths.

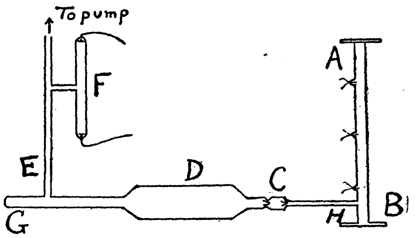

Fig. 9.

Purity of the Metals.—The sodium and potassium were purchased from Eimer and Amend and, in a personal letter from the company, were claimed to be "very pure." I am indebted to Dr. G. McP. Smith, of the chemistry department, for the following test on the purity of these metals.

Sodium.

1. Free from iron (KCNS test).
2. Free from calcium ($(NH_4)_2C_2O_4$ test).
3. Free from magnesium (Na_2HPO_4 test).
4. Free from aluminum (no ppt. with NH_4OH–Na_2HPO_4 test).
5. Free from potassium (H_2PtCl_6 test).

Spectroscopic test also negative, but conditions were not most favorable at time of test.

Potassium.

1. Free from iron.
2. Free from calcium.
3. Free from magnesium.
4. Free from aluminum.
5. Contains enough sodium to give a test with the spectroscope. Undoubtedly only a trace.

Method of Control of Temperatures.—The apparatus for controlling temperatures has been described in Chapter III. For the determinations above room temperature, the temperatures were adjusted and held constant by means of Bunsen flames, one under each end-bath and three beneath the large reservoir from which the water was pumped through the brass jacket. For the lower temperatures the turbine was discarded and cold water was run through the jacket by gravity pressure, the rate of flow being regulated by a small globe valve. In these determinations the temperatures of the end baths were watched constantly by a student helper and were maintained by the continuous addition of snow and salt.

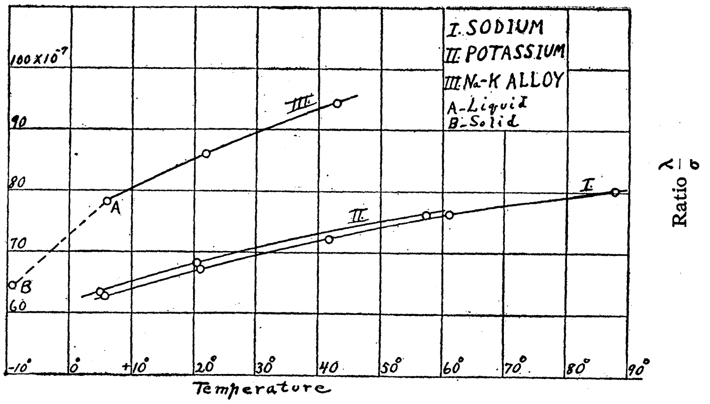

Fig. 10.

Regulation of the Heating Current.—As already mentioned, the currents from the large storage battery were remarkably constant. The slight regulation necessary was accomplished with a mercury rheostat. The U-tube, which was made of glass tubing 2.6 cm. in diameter, stood 80 cm. high. Continuous adjustments could be made by varying the position of the copper-plated iron rods which dipped into the mercury.

V. Data Tables and Curves.

In order to cut down the length of the paper the original data will be given only for a few typical runs. They will serve to illustrate the method

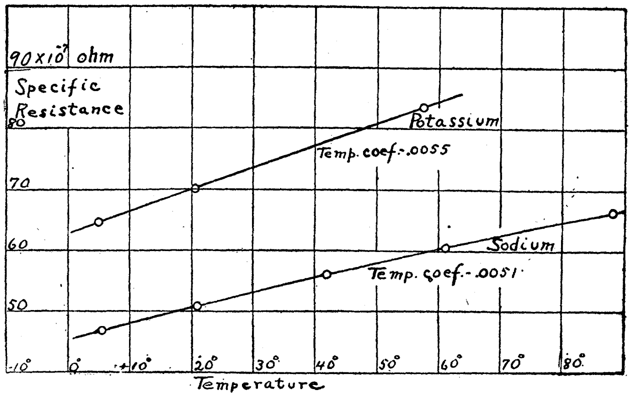

Fig. 11.

of taking observations and to indicate the degree of consistency obtained at different temperatures. In the tables which follow these "specimen runs," merely the final results are recorded.

Meaning of Symbols.—In all the data tables the following notation is used:

r_1, r_3 = balance-resistance on potentiometer dial for thermo-couples No. 1 and No. 3.

r_2 = balance-resistance for thermo-couple No. 2 at middle of tube (or rod).

r' = balance-resistance when reading P.D.

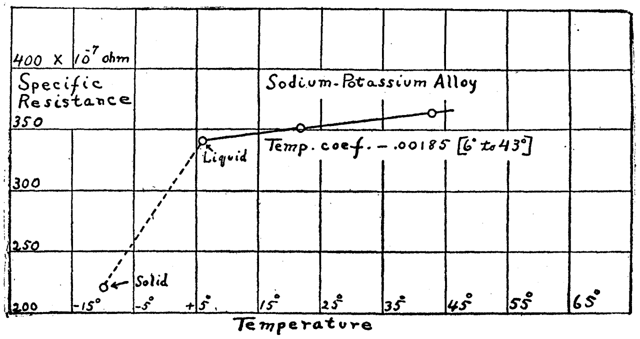

Fig. 12.

u_1, u_2, u_3 = temperatures corresponding to resistances r_1, r_2, r_3.

u_0 = temperature of the brass jacket.

$u' = \frac{1}{2}(u_1 + u_3)$.

$t_m = \frac{1}{2}(u' + u_2)$ = temperature for which the values of σ/λ, ρ and λ are taken in plotting curves.

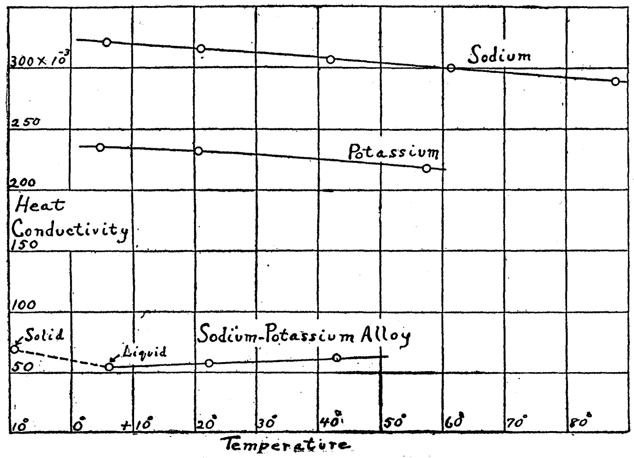

Fig. 13.

V = one-half of the P.D. between the two points which were held at the same temperature.

I = value of heating current in amperes.

$\Delta = u_2 - u'$. $U = \Delta - \epsilon N$.

$N = u_0 - u_2 + \frac{1}{6}\Delta$. $\epsilon = \Delta/N$ when $I = 0$.

The letters D and R in the tables represent direct and reversed currents through the potentiometer to eliminate contact potential differences.

No. 2606 and No. 2607 refer to the two Beckmann thermometers which gave the temperature of the brass jacket.

TABLE I.

Constants for the Three Tubes.

Substance.	Inside Diameter.	Area a.	Effective Length l.
Na-K Alloy	1.562 cm.	1.916	20 cm.
Potassium	1.620 cm.	2.061	20 cm.
Sodium	1.234 cm.	1.196	20 cm.

$$\rho = \frac{Ra}{l} = .0958R = \frac{.0958 \times 2V}{I}, \text{ for sodium-potassium alloy.}$$

$$\rho = \frac{0.103 \times 2V}{I}, \text{ for potassium tube.}$$

$$\rho = \frac{.0598 \times 2V}{I}, \text{ for sodium tube.}$$

TABLE II.

Correction Factor for Potassium Tube (Specimen Run).

	r_1	r_3	r_2	u_0 No. 211.	u_0 No. 212.
D	187.8	187.7	197.2	2.20	1.36
R	186.8	186.8	196.2		
D	187.5	187.8	197.0	2.18	1.35
R	186.6	186.9	196.2		
D	187.5	187.8	197.0	2.19	1.30
R	186.7	186.9	196.3		
D	187.5	187.6	196.9	2.20	1.27
R	186.7	186.7	196.2		
D	187.1	187.8	196.9	2.23	1.24
R	186.4	186.9	196.1		

Left bath held at 18.4°; right bath at 18.3°.

Mean temperature on No. 211 = 2.20 + 33.06 = 35.26°.

Mean temperature on No. 212 = 1.30 + 32.91 = 34.21°.

$u_0 = \frac{1}{2}(35.26 + 34.21) = 34.74°$ C.

Mean r_1 = 187.1 ohms; $u_1 = 20.025°$.

Mean r_3 = 187.3 ohms; $u_3 = 19.965°$.

Mean r_2 = 196.6 ohms; $u_2 = 20.925°$.

$\Delta = 20.925 - 19.955 = 0.930°$.

$N = 34.74 - 20.925 + 0.155 = 13.97°$.

$$\epsilon = \frac{\Delta}{N} = \frac{0.930}{13.97} = .066.$$

Table III.

Sodium-Potassium Alloy at 5.7° (Specimen Run).

	Main Current Direct.					Main Current Reversed.				
	r'	r_1	r_3	r_2	u_0 No. 2606.	u_0 No. 2607.	r_1	r_3	r_2	r'
D	3667	33.9	35.9	68.4	4.05	4.30	34.9	35.7	68.8	3661
R		35.2	37.3	69.8	4.10	4.25	36.2	37.2	70.2	
D	3656	34.2	35.9	68.5	3.95	4.15	34.9	35.6	68.4	3664
R		36.0	37.3	69.9	3.95	4.20	36.7	37.2	70.3	
D	3656	34.2	35.9	68.6	3.94	4.20	34.8	35.5	68.4	3661
R		36.0	37.4	70.0	3.90	4.15	36.8	37.2	70.4	
D	3657	34.2	35.9	68.4	3.95	4.15	34.6	35.4	68.2	3663
R		36.1	37.6	70.2	3.93	4.15	36.6	37.2	70.2	
D	3658	34.1	35.7	68.3	3.98	4.17	34.6	35.4	68.1	3662
R		35.9	37.6	70.1	3.93	4.15	36.6	37.2	70.1	

Left bath at – 0.4°; right bath at 0°.
6 volts, 6 sets in parallel. $I = 41.2$ amp.
Mean $r_1 = 35.4$ ohms; $u_1 = 4.02°$. Mean reading on No. 2606 = 3.97.
Mean $r_3 = 36.6$ ohms; $u_3 = 4.04°$. Mean reading on No. 2607 = 4.20.
Mean $r_2 = 69.3$ ohms; $u_2 = 7.42°$.

$$\left.\begin{array}{l}\text{Mean temp. on No. 2606} = 3.97 + 2.41 = 6.38° \text{ C.}\\ \text{Mean temp. on No. 2607} = 4.20 + 2.76 = 6.96° \text{ C.}\end{array}\right\} u_0 = 6.67° \text{ C.}$$

Mean $r' = 3{,}660$ ohms. $2V = 3660 \times 4 \times 10^{-6} = .01464$ volt.

Sample Calculation.

$$\Delta = 7.42 - 4.03 = 3.39. \quad t_m = \tfrac{1}{2}(4.03 + 7.42) = 5.7°.$$

$$N = u_0 - u_2 + \tfrac{1}{6}\Delta = 6.67 - 7.42 + 0.57 = -0.18.$$

$$U = \Delta - \epsilon N = 3.39 + 0.22 \times 0.18 = 3.43.$$

$$\frac{\sigma}{\lambda} = \frac{2U}{V^2} = \frac{6.86}{(.00732)^2} = 128.1 \times 10^3.$$

$$\rho = \frac{.0958 \times .01464}{41.2} = 34040 \times 10^{-9} \text{ ohm.}$$

$$\lambda = \frac{10^5}{4.19 \times 128.1 \times 3404} = .0547 \text{ cal.}$$

Table IV.

Sodium at Room Temperature (Specimen Run).

	Main Current Direct.					Main Current Reversed.				
	r_1	r_3	r_2	r'	u_0 No. 2606.	u_0 No. 2607.	r_1	r_3	r_2	r'
D	187.6	190.9	218.0	3096	5.40	5.48	187.6	188.9	217.1	3099
R	187.0	190.3	217.4				188.7	188.0	217.9	
D	188.3	190.5	218.0	3093	5.43	5.52	187.7	188.9	217.3	3098
R	187.3	189.6	217.2				189.5	187.9	218.2	
D	188.7	190.9	218.6	3093	5.48	5.56	188.2	189.0	217.6	3098
R	187.7	190.3	217.6				189.3	188.2	218.4	
D	188.2	190.9	218.5	3093	5.53	5.61	188.1	188.9	217.4	3098
R	187.4	190.2	217.5				189.4	188.1	218.2	

12 volts, 12 sets in parallel. $I = 146.3$ amp.
Left bath held at 14.8°; right bath held at 15.9°.

Mean r_1 = 188.2; u_1 = 20.08°. Temp. on No. 2606 = 5.46 + 18.08 = 23.54.
Mean r_3 = 189.5; u_3 = 20.12°. Temp. on No. 2607 = 5.54 + 18.05 = 23.59.
Mean r_2 = 217.8; u_2 = 23.01. u_0 = 23.57° C.
Mean r' = 3,096 ohms. $2V = 3{,}096 \times 4 \times 10^{-6}$ = .01238 volt.
Δ = 2.91. N = 1.05. U = 2.85°. t_m = 21.5°.

TABLE V.

Potassium at 57.8° (Specimen Run).

	Main Current Direct.					Main Current Reversed.				
	r'	r_1	r_3	r_2	u_0 No. 2606.	u_0 No. 2607.	r_1	r_3	r_2	r'
D	3075	560.6	554.4	584.5	3.38	2.75	557.6	558.4	584.4	3070
R		559.0	556.2	582.6	3.37	2.76	556.0	559.8	583.0	
D	3071	556.0	553.5	582.8	3.38	2.76	555.7	557.9	583.6	3070
R		557.8	555.2	581.0	3.42	2.77	553.8	559.6	582.0	
D	3078	557.4	554.9	584.1	3.43	2.78	557.7	557.6	584.3	3069
R		558.9	556.7	582.3	3.48	2.81	555.4	559.7	582.4	
D	3078	553.6	555.9	584.3	3.42	2.83	558.1	555.3	584.3	3079
R		555.3	560.6	582.5	3.35	2.81	555.6	557.1	582.4	
D	3074	554.4	555.9	584.4	3.27	2.73	557.8	555.2	584.0	3074
R		556.2	558.6	582.6	3.25	2.70	555.4	557.0	582.2	

16 volts, 8 sets in parallel. $I = 148.1 \times 1.026$ = 152.0 amp.
Left bath at 51.0°. Right bath at 51.3°.
Mean r_1 = 556.6; u_1 = 56.625°. Temp. on No. 2606 = 3.38 + 54.98 = 58.36.
Mean r_3 = 557.4; u_3 = 56.630°. Temp. on No. 2607 = 2.77 + 55.13 = 57.90.
Mean r_2 = 583.2; u_2 = 59.070°. u_0 = 58.13°.
Mean r' = 3074 ohms. $2V$ = .012296 volt.
Δ = 2.443°. N = − 0.53. U = 2.478°. t_m = 57.8°.

TABLE VI.

Values of Correction Factor ϵ.

Substance.	u_0	u_2	Δ	N	ϵ
Lead rod	21.7	16. 7	0.918	5.38	0.171
Na-K alloy	21.19	15.40	1.35	6.01	0.224
	24.46	19.86	1.02	4.77	0.214
Potassium	34.74	20.925	0.930	13.970	0.066
Sodium	41.80	18.66	1.38	23.37	0.059

TABLE VII.

Complete Results for Lead (Commercially Pure).

Run No.	u_0	u_2	t_m	$2V$ $10^{-5}\times$	Δ	N	U	I Amp.	σ/λ $10^3\times$
1	21.64	21.94	20.6	1253	2.671	0.14	2.647	51.0	134.6
2	21.65	23.60	21.7	1566	3.838	−1.32	4.062	63.3	132.5
3	21.71	23.28	21.3	1588	4.046	−0.90	4.199	64.3	133.2

Remark.—For run No. 3, the lead rod was inside of a close-fitting glass tube.

Table VIII.

Complete Results for Sodium-Potassium Alloy.
(Masses taken proportional to the atomic weights.)

Run No.	u_0	u_2	t_m	$2V$ $10^{-5}\times$	Δ	N	U	I Amp.	σ/λ $10^3\times$	ρ Ohm $10^{-8}\times$	λ Cal.
1	−8.30	−8.28	−10.6	1511	4.56	+0.74	4.40	66.0	154.4	2193	.0705
2	−9.40	−6.37	− 8.9	1682	5.00	−2.20	5.48	72.9	155.2	2210	.0696
3	+6.67	7.42	5.8	1464	3.39	−0.18	3.43	41.2	128.1	3404	.0547
4	6.66	8.07	6.2	1588	3.83	−0.77	4.00	44.6	127.0	3411	.0551
5	22.40	23.936	22.0	1684	3.931	−0.88	4.122	45.9	116.3	3515	.0584
6	22.54	24.075	22.1	1702	4.003	−0.86	4.190	46.2	115.9	3527	.0584
7	22.66	22.395	20.7	1500	3.453	+0.84	3.271	40.9	116.2	3513	.0585
8	43.90	44.54	42.9	1550	3.17	−0.11	3.19	40.8	106.1	3640	.0619

Table IX.

Complete Results for Potassium.

Run No.	u_0	u_2	t_m	$2V$ $10^{-5}\times$	Δ	N	U	I Amp.	σ/λ $10^3\times$	ρ Ohm $10^{-8}\times$	λ Cal.
1	5.91	5.790	5.0	881	1.557	+0.38	1.531	141.9	158.2	649.2	0.232
2	6.58	5.810	5.0	862	1.525	+1.02	1.454	137.9	156.5	644.2	0.237
3	21.16	21.670	20.7	1035	1.965	−0.18	1.978	151.6	147.7	703.5	0.230
4	21.22	21.590	20.6	1030	1.920	−0.05	1.923	151.2	145.1	701.5	0.234
5	21.45	21.675	20.9	932	1.603	+0.04	1.600	137.6	147.4	698.0	0.232
6	58.13	59.070	57.8	1230	2.443	−0.53	2.478	152.0	131.1	833.8	0.218
7	57.91	58.510	57.4	1184	2.312	−0.21	2.326	147.3	132.4	835.3	0.216

Table X.

Complete Results for Sodium.

Run No.	u_0	u_2	t_m	$2V$ $10^{-5}\times$	Δ	N	U	I Amp.	σ/λ $10^3\times$	ρ Ohm $10^{-8}\times$	λ Cal.
1	7.20	6.97	5.7	1152	2.68	+0.68	2.64	147.7	159.0	466.4	0.321
2	7.75	7.22	5.8	1176	2.82	+1.00	2.76	150.7	159.5	466.7	0.321
3	23.42	22.12	20.9	1110	2.385	+1.70	2.283	130.6	148.2	508.3	0.317
4	23.57	23.01	21.5	1238	2.91	+1.05	2 85	146.3	148.8	506.0	0.317
5	43.32	43.44	42.1	1207	2.57	+0.31	2.55	128.3	139.7	562.6	0.304
6	44.97	43.38	41.7	1360	3.32	+2.14	3.19	145.5	138.1	559.0	0.309
7	62.30	62.84	61.3	1390	3.15	+0.01	3.15	137.2	130.4	605.8	0.302
8	63.11	62.83	61.4	1320	2.93	+0.77	2.88	130.7	132.1	604.0	0.299
9	89.01	89.43	88.1	1309	2.67	+0.03	2.67	118.0	124.8	663.4	0.288

VI. Discussion of Results.

In using the experimental method of obtaining the value of the correction factor ϵ for the alkali metals, it was necessary to assume that for the steady state the temperatures at corresponding points on the inside and outside surfaces of the glass tube were equal; *i. e.*, that the temperature gradient through the walls of the glass tube could be neglected in comparison with the drop in temperature through the cotton wool. One reason for making the runs with the lead rod was to find out if this assumption would introduce an error large enough to be detected. Table VII. answers the question. The fact that the value of σ/λ for run No. 3 falls between those for runs No. 1 and No. 2, proves that the effect of surrounding the rod with the glass was smaller than other experimental errors. Lead was chosen for this experiment because of its low heat conductivity. The glass wall would have a still smaller effect in case of the sodium and potassium.

Another reason for taking the data for lead was to have a means of comparing my results with those of Jaeger and Diesselhorst. In this connection it should be noted that my average value of σ/λ for lead at 21.5° is 133.4×10^3 while that of Jaeger and Diesselhorst for pure lead, when reduced to 21.5°, is 138.2×10^3. This was considered a good check because the lead I used was only commercially pure. The presence of impurities always reduces the value of σ/λ.

As to accuracy of results it should be pointed out that for each run steady conditions were held for one to two hours and readings were taken continually during this time. Thus each value of u_1, u_2 and u_3, used in the calculations, depends upon sixteen to twenty readings on the potentiometer, while the values of V are computed from the mean of eight to ten readings. The current could be maintained much more nearly constant than could the temperatures and therefore the potential difference did not need to be read so often. Moreover, with one or two exceptions, every point on the curves represents the mean result of two or three independent runs.

The curves for λ/σ bend more than was expected. It would be interesting to know whether they become straight lines at higher temperatures. Judging from the behavior of other metals, this should be expected. Moreover, when $\lambda/\sigma T$ is plotted against T, these curves slope downward slightly with increasing temperature while Lees's curves for most of the pure metals bend slightly upward at ordinary temperatures. Thus sodium and potassium, like nickel, are irregular in this respect. It should be noted that the heat conductivities of sodium and potassium decrease slightly with increasing temperature, while the heat conductivity of the alloy *increases* with the temperature. This is the law followed by most metals and their alloys. The temperature coefficients of sodium and potassium are extremely high.

The mean values of the specific resistance of sodium and potassium at room temperature and the temperature coefficients are given below for convenience of comparison.

spec. res. of Na at 21.7° C. = 5072×10^{-9} ohm/cm.^{3}.
spec. res. of K at 20.7° C. = 7010×10^{-9}
temp. coef. of Na = .00513, range 6° to 88°
temp. coef. of K = .00552, range 5° to 58°

Northrup's Results.

spec. res. of Na at 20° C. = 4873×10^{-9}
spec. res. of K at 20° C. = 7116×10^{-9}
temp. coef. of Na = .0053, range 20° to 80°
temp. coef. of K = .0058, range 20° to 50°

Matthiesen's Result.

spec. res. of Na at 21.7° C. = 4464×10^{-9}

Bernini's Results.

spec. res. of Na at 0.0° = 4739×10^{-9}
spec. res. of K at 0.0° = 6644×10^{-9}

Bernini's results, when reduced to room temperature, are found to be higher than mine and Northrup's, while Matthiessen's value is seen to be lower. It is thought that my results agree with Northrup's as closely as could be expected, considering the wide difference in method. Indeed his method is the more accurate one for electrical conductivity. Consequently, the results of this investigation may be said to confirm Northrup's work on the resistance of sodium and potassium. The slightly smaller values of the temperature coefficients suggest that the metals used in this work may not have been quite as pure as those Northrup used.

SUMMARY.

1. The electrical conductivities of sodium, potassium and sodium-potassium alloy have been measured and the results are in agreement with the values obtained by Northrup.
2. The heat conductivities of the alkali metals have been measured for the first time, as far as known.
3. The temperature coefficients of these conductivities have been determined.
4. The resistance-temperature coefficients of potassium and sodium are extremely high.
5. The values of the ratio σ/λ for the alkali metals are extremely high.
6. The alkali metals behave in no exceptional way as regards the absolute values of the thermal and electrical conductivities at ordinary temperatures.
7. As a check on the method, the ratio σ/λ was determined for lead at room temperature and the value agrees with the one obtained by Jaeger and Diesselhorst.
8. A modification of the electron theory of metallic conduction has

been suggested which accounts for the variation of the specific heat with the temperature, and also explains the curves which Lees obtained for the ratio $\lambda/\sigma T$ for the pure metals at low temperatures.

In conclusion, I wish to acknowledge my indebtedness to Professor A. P. Carman, who has followed this work with continued interest, placing at my disposal all the facilities necessary for the investigation; and to Professor Jakob Kunz, under whose direction the work was done, for many good suggestions and for invaluable assistance in filling the tubes. I also wish to thank Dr. G. McP. Smith, of the chemistry department, who analyzed the metals used in this investigation.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
May, 1913.

Note.—Since this paper was written, I note in the April number of Science Abstracts, which has just come, that W. Wien has published an article on "Electric Conduction in Metals" based upon the "quanta hypothesis." His theory may be similar to the modification suggested in this paper. The article referred to is not accessible in our library.

J. W. H.