THERMAL CONDUCTIVITY OF Li AND Na BY A MODIFICATION OF THE FORBES BAR METHOD[1]

By C. C. Bidwell

Abstract

The bar method of Forbes was modified as follows. The metal rod, centered in a large test tube, was placed in a constant temperature bath and heated by a coil at the upper end. Convection in the tube was stopped by cardboard disks through which the rod was threaded and which were spaced at short intervals along the rod. Temperature gradient was determined by thermo-junctions spaced along the rod. Cooling curves were obtained on smaller lengths of the rod similarly mounted. With mean temperature not exceeding 15° above bath temperature accurate values of k were obtained.

Lithium shows a linear increase in k from 0.15 at 0°C to 0.20 at -200°C, thereafter rising sharply to 1.00 at -246°C. Above 0°C a minimum occurs at $+40$°C and an increase thereafter to 0.17 at $+140$°C. Sodium shows a linear increase from 0.28 at -40°C to 0.40 at -240°C. Above -40°C an increase occurs to 0.34 at 0°C and thereafter a decrease to 0.28 at $+65$°C. The breaks in these lines correspond to breaks previously reported in electrical resistance and thermo-electric power lines for these metals.

Electrical conductivity of Li and Na. To test the Wiedemann-Franz-Lorentz law the resistances of wires of lithium and sodium were measured at temperatures of ice, liquid oxygen and liquid hydrogen. The "constant" $k/\sigma T$ of the Wiedemann-Franz law was found to have at the higher temperatures the value predicted by the Lorentz theory, and to diminish steadily with temperature in accord with more modern theory.

Specific heats of Li and Na. The specific heats of Li and Na were calculated by a comparison of cooling curves. The values found are in agreement with the best previous measurements and are extended to liquid hydrogen temperatures. At the higher temperatures the atomic heats of both metals exceed the Dulong and Petit maximum. It is suggested that this excess is latent heat of crystallization. At the lower temperatures the results do not show agreement with the Debye specific heat equation.

Introduction

THE measurement of the temperature gradient along a bar of metal together with an auxiliary determination of the rate at which heat escapes from each section, obtained by means of cooling curves, makes possible, in theory, a direct computation of thermal conductivity. The method was first used by Forbes[2] and modifications were made later by

[2] Forbes, Trans. Roy. Soc. Edin. **23**, 133–146 (1865); **24**, 73–110 (1865).

Mitchell[3] and by Stewart.[4] Since these early observers failed to get precise results, a comparison of their procedure with that used in the present investigation is of interest. Forbes used a wrought iron rod eight feet long arranged horizontally in the open air with one end extending into a bath of molten lead. Temperatures were read by mercury thermometers placed in mercury wells. With a rod one inch in diameter he got values differing by 20% from those obtained with a rod 1.25 inches in diameter. J. C. Mitchell under Tait's direction repeated Forbes' work using the same rod and correcting for the variation in specific heat, which Forbes had ignored, and cooling the far end of the bar in water. With the rod thus cooled values did not agree with those obtained when not cooled, the variation being about 10% sometimes more, sometimes less. Stewart substituted insulated thermo-couples and made an effort to protect the bar from drafts by placing a trough under it. The Encyclopedia Brittainica, 11th Ed., in its discussion of the bar methods, says, "The discrepancies are chiefly due to the error of the fundamental assumption that the rate of cooling is the same at the same temperature under the very different conditions existing in the two parts of the experiment." The use of mercury thermometers and of insulated thermo-junctions must have contributed also to the discrepancies in all this early work.

The Forbes method is departed from in the bar experiments of Callender and Nichols[5] and of Lees[6] in which heat escape from the sides of the bar is eliminated either by lagging or by placing the rod in a vacuum. Callender and Nichols used a bar 4 feet long and with a diameter of 4 inches. One end was placed in steam the other in running water, the rise in temperature of which was measured. Lees used a short rod 8 cm long, .585 cm in diameter, surrounded it with packing and heated one end electrically. The other end was fitted into a copper block. Temperatures at top and bottom of the rod were measured by platinum resistance wires wound on the rod. Schott[7] modified Lees method by placing the rod in a vacuum. Good results were obtained by all these observers.

In the present study wide departures were made from the procedure of the early observers although the method in theory is exactly that of Forbes. The special features to be emphasized are (1) exact duplication of the external conditions in the two parts of the experiment, (2) precise temperature measurements through the use of bare thermo-couples

[3] Mitchell, Trans. Roy. Soc. Edin. **28**, 717 (1879)
[4] Stewart, Phil. Trans. Roy. Soc. London **184A**, 570 (1893)
[5] Callender and Nichols, Ency. Britt. 11th Ed.
[6] Lees, Phil. Trans. **208**, 381 (1908).
[7] Schott, Verh. d. D. Phys. Ges. **18**, 27 (1916).

embedded in the rod and in metallic contact with it, (3) development of the theory leading to equations which fit exactly the experimental conditions and whose terms can be precisely evaluated from the experimental data by graphical or analytical methods.

The metals investigated were sodium, lithium, and single and poly-crystal zinc. The present report deals only with the work on sodium and lithium. Rods of these metals 25 cm long and 1.10 cm in diameter, produced by extrusion through a die, were mounted in glass tubes as shown in Fig. 1. A heater coil consisting of about 10 turns of chromel A
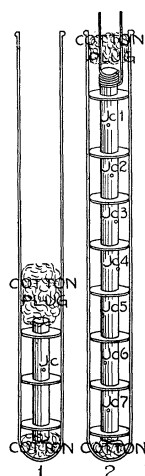

Fig. 1. 1. Arrangement for getting cooling data.
2. Arrangement for getting gradient data.

resistance wire No. 26 was wound on the upper end of the rod but insulated from it by several layers of oiled paper. Copper-constantan thermo-junctions (No. 30 wire) were spaced every 3 cm along the rod. The bare junctions were pressed into the soft metal by means of a needle to a depth of 2 or 3 mm and the needle hole closed by squeezing the metal back about the wires. Tissue paper insulation wound on the junction wires insulated them from each other and from the rod. Usually six junctions were placed on a rod. After the junctions were mounted cardboard washers were slipped over the rod and spaced every two cm along the rod. These washers fitted the rod tightly and were of such outer diameter as also to fit snugly the glass tube in which the rod was mounted. They served to center the rod and to cut off convection currents up and down the tube. The glass tube containing the specimen thus mounted was 2.7 cm in diameter, 40 cm in length, and closed at the lower end. The

tube was used in a vertical position with the rod in the lower half. The heater leads and all junction leads were led out through the top of the tube. The tube with the rod thus mounted was placed in a constant temperature bath contained in a Dewar cylinder of 40 cm length and some 7 cm inside diameter. The bath usually extended about 15 cm above the top of the rod. The tube above the rod was stuffed with cotton. (In the case of the liquid hydrogen bath a shorter tube was used, one which did not extend much above the bath level and which therefore did not allow the entrance of air which would have liquified and frozen about the specimen). The constant temperature baths were liquid hydrogen, -252.8°; liquid oxygen, -183°; CO_2 slush, -77.5°; crushed ice, 0°; boiling chloroform, +61°; boiling water, +100°; boiling tetrachlorethelene, +121°.

The rod was allowed to come to the temperature of the bath and the readings of all junctions were taken. Then the rod was heated at the top by means of the resistance coil until the top junction read about 3° or 4° above the bath temperature and the current was adjusted to hold this temperature. Readings of all junctions were taken at intervals until equilibrium was established and no further changes were found to occur. About one hour usually sufficed, although at liquid hydrogen temperature five minutes was sufficient. After all readings were taken the heater current was increased until the top junction read 10° or 15° above bath temperature and the operation repeated. Thus two sets of readings were obtained for each bath. After these data were obtained the rod was, where conditions permitted, removed from the tube and immersed directly in the bath and the readings of each junction obtained, the heater current of course being zero. This gave the reading of each junction for the bath temperature thus permitting discrepancies in junction readings to be determined and taken into account.[8]

For the second parts of the experiment a short rod, in most cases 4 cm long, of exactly the same diameter as the test rod, containing a single junction embedded in it and similarly fitted with cardboard washers, was preheated 60° to 80° above the bath temperature then slipped into the tube and allowed to cool to the bath temperature. Temperatures were read every half minute as the rod cooled. For each bath cooling curves were thus taken on rods of lithium, sodium, copper, lead and

Temperatures along the rod were determined by a method of differences. The difference in microvolts between the bath temperature and the rod temperature as expressed by the same junction was divided by the microvolts per degree for the particular temperature obtained from the calibration equation of the junction. Relative temperatures along the rod were accurate within .05°, although actual temperatures may have been uncertain within one or two degrees.

silver, each rod being of the same dimensions and similarly mounted. To obtain similar surfaces all rods were wound tightly with a single layer of paper. Cooling curves were also obtained with copper and lead rods of 8 cm length. Exactly the same heat loss rate per cm length was obtained in these cases. The determination of the rate of heat loss per cm length is the critical part of the work and for that reason the observations were
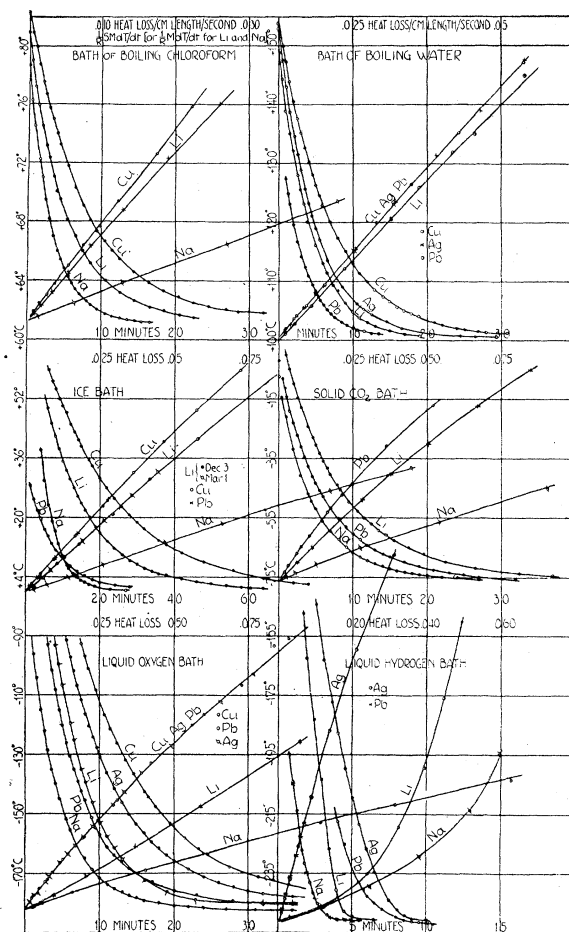

Fig. 2. Cooling and heat loss curves for different metals at various bath temperatures.

obtained on these various metals so that the heat loss curves might be very accurately established. All the rods had the diameter 1.10 cm. *A* rod of 1 cm diameter gave quite a different heat loss rate per cm length and even per sq cm, apparently because of the longer air path through

which the heat must be carried to the surrounding tube. The same surrounding tube was used in all cases as tubes of slightly different diameters caused serious discrepancies. Cotton plugs above and below the cooling specimen eliminated heat loss from the ends. This was proven by the fact that the heat loss per cm length from the 8 cm rod was exactly the same as from the 4 cm rods. Fig. 2 shows the cooling curves and the heat loss curves derived from them for the different metals and for the various bath temperatures. Rate of heat loss per cm length is computed from the formula $Ms/L \cdot dT/dt$, where L is the length of the specimen, M its mass, s, the specific heat and dT/dt the rate of cooling.
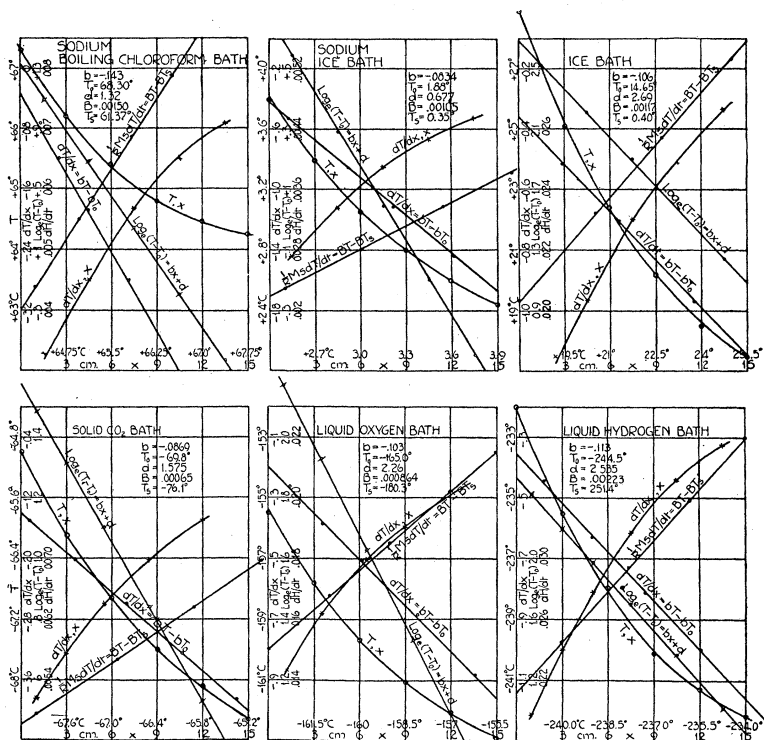

Fig. 3. Gradient data and derived relations for sodium.

THEORY OF THE METHOD

The difference between the heat which flows through a given section of the rod a distance x_1 from some arbitrary origin near the hot end and that which flows through a section a distance x_2 from the same origin is equal to the heat which escapes from the surface between the two sections. This is expressed by the equation
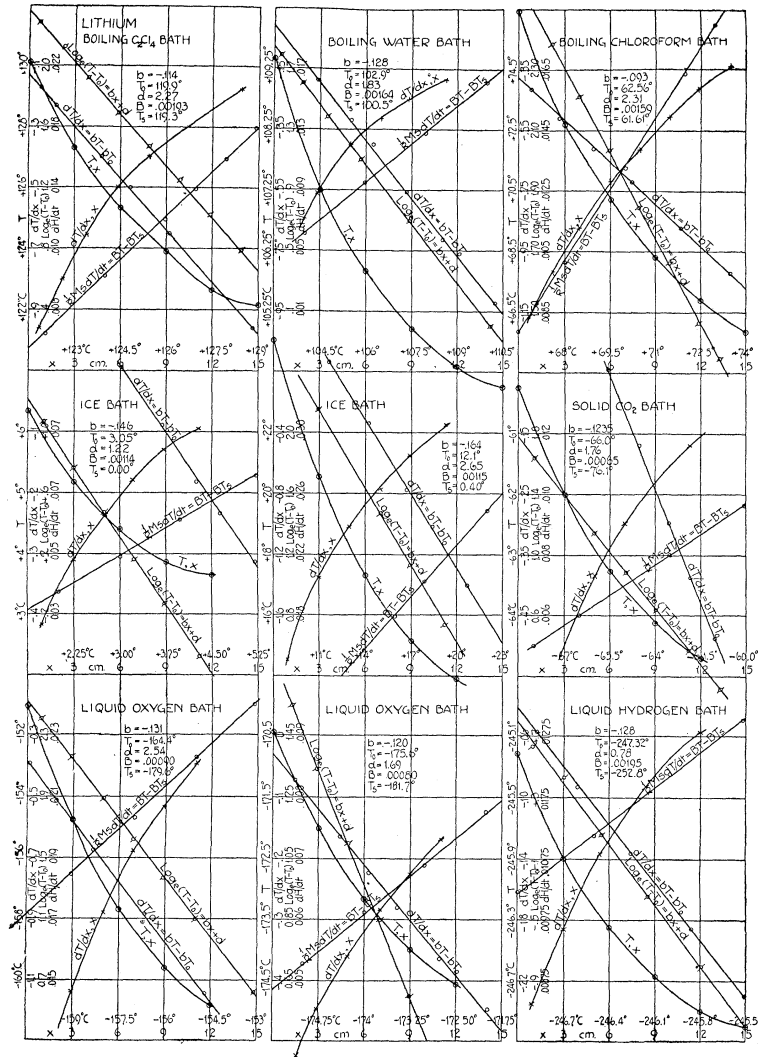
Fig. 4. Gradient data and derived relations for lithium.

$$kA\left[(dT/dx)_1-(dT/dx)_2\right]=\int_{x1}^{x2}(dH/dt)dx \tag{1}$$

k is the thermal conductivity; A, the cross-section of the rod; $(dT/dx)_1$ and $(dT/dx)_2$, the temperature gradients at points x_1 and x_2; (dH/dt), the heat loss per second per cm length. (dH/dt) may be obtained from the cooling data and is given by the expression $dH/dt = Ms/L \cdot dT/dt$. Fig. 2

shows that over short temperature ranges the heat loss curves are sensibly straight lines. The temperature drop along the rods rarely exceeded 10° and in most cases did not exceed 3° whereas the heat loss curves are essentially straight lines over 20° or more. Thus we may write

$$Ms/L \cdot dT/dt = BT + D$$

or

$$Ms/L \cdot dT/dt = BT - BT_s \tag{2}$$

We may call T_s the apparent surrounding temperature. It is the actual surrounding temperature only when the average value of T is within a few degrees of the bath temperature or when the temperature interval is the first interval on the heat loss curve. Eq. (1) now becomes

$$kA[(dT/dx)_1 - (dT/dx)_2] = \int_{x1}^{x2} BT dx - \int_{x1}^{x2} BT_s dx \tag{3}$$

Figs. 3 and 4 show T, the temperature along the rod, plotted against x, the distance along the rod measured from the first junction as origin; also dT/dx, the slopes of these lines plotted against temperature. These are shown for the various bath temperatures. The dT/dx, T curves are in all cases straight lines. Therefore

$$dT/dx = bT + a$$

or

$$dT/dx = bT - bT_0 \tag{4}$$

This equation may be written

$$\int dT/(T - T_0) = \int b dx \text{ which gives}$$

$$\text{Log}_e(T - T_0) = bx + d \tag{5}$$

or

$$T = e^{bx+d} + T_0 \tag{6}$$

The lines representing Eq. (5) are also shown on Figs. 3 and 4. Using Eq. (6) in (3) we have

$$kA[(dT/dx)_1 - (dT/dx)_2] = \int_{x1}^{x2} B[e^{bx+d} + T_0]dx - \int_{x1}^{x2} BT_s dx. \tag{7}$$

This becomes

$$kA[(dT/dx)_1 - (dT/dx)_2] = \frac{Be^d}{b}[e^{bx_2} - e^{bx_1}] + B(T_0 - T_s)[x_2 - x_1] \tag{8}$$

The constants B, d, b, T_0 and T_s of this equation may be obtained graphically from the curves of Figs. 3 and 4. Thus with the gradients known at distances x_1 and x_2, k may be computed.[9]

[9] T_0 (Eq. 4) is the temperature of the rod where the gradient is zero. This has physical significance as such only when the rod is very long or when the mean rod temperature is only slightly above the bath temperature. In such cases $T_0 = T_s =$ bath temperature, and the last term of Eq. (8) vanishes, but with short rods and higher rod temperature, this term is increasingly important.

RESULTS

The values of thermal conductivity, k, as a function of temperature are shown for sodium in Fig. 5 and for lithium in Fig. 6. In the case of lithium
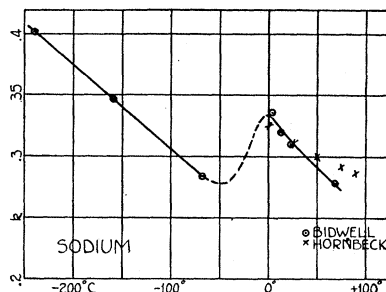

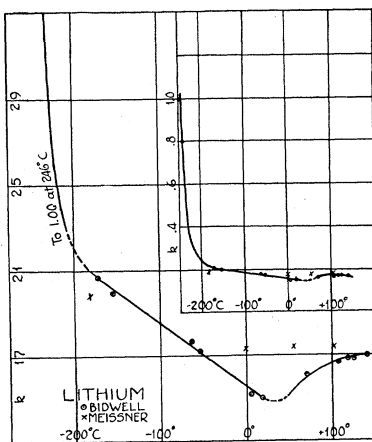Fig. 5. Thermal conductivity of sodium.

Fig. 6. Thermal conductivity of lithium.

two values were obtained for each bath. In one case the average temperature of the rod was not more than 5° above bath temperature, in the other the average temperature was 10° or 15° above bath temperature. The values of the constants B, d, b, T_0 and T_s are entirely different in the two cases yet the equation gives consistent values for k in each case. We have thus an excellent check on the method and on the computations. The discontinuities shown on these curves, at $-50°$ for sodium and at $+40°$ for lithium are extremely interesting especially in view of the resistance and thermoelectric power behavior in these same regions. Fig. 7 reproduced from a previous paper[10] shows the electrical resistance and thermoelectric

[10] Bidwell, Phys. Rev. 23, 357 (1924).

power lines for these metals. It will be noted that these lines indicate changes or discontinuities in the same temperature regions. Comparison of Figs. 5 and 6 leads to the view that the change in the case of sodium is practically completed in the region -50° to 0° whereas in the case of lithium the transition is more gradual extending over the range +40° to at least +150° where the value of k seems to have reached a maximum. From the behavior of the sodium line one would predict a decrease in k for lithium above +150°C but data on this are not yet available and
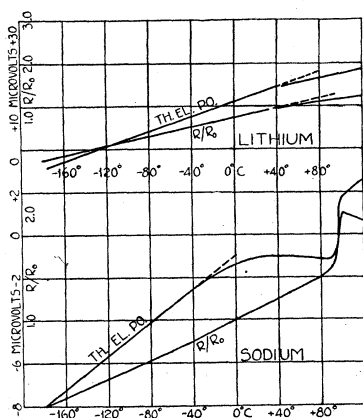

Fig. 7. Electrical resistance and thermoelectric power of lithium and sodium.

are not obtainable by the present method. The discontinuities in these lines are apparently associated with the breakdown of the crystal lattice. That the lattice structure becomes obliterated at the higher temperatures for these metals has been shown by the writer[11]. An increase in thermal conductivity associated with a disintegration of the crystal lattice is an observation which should have a fundamental bearing on the theory of heat conduction.

THE WORK OF OTHER OBSERVERS ON LITHIUM AND SODIUM

The only other work with which the present observations may be compared is that of Meissner[12] on lithium and Hornbeck[13] on sodium. Both of these observers used the Kohlrausch-Diesselhorst Method. In this method a wire or rod of the metal is mounted in a highly exhausted tube, the ends of the rod or wire kept at constant temperature, and a temperature gradient established by an electric current sent through the·

[11] Bidwell, Phys. Rev. **27**, 381 (1926).
[12] Meissner Zeits. f. Physik **2**, 273 (1920)
[13] Hornbeck, Phys. Rev. **2**, 217 (1913).

rod or wire. Hornbeck measured the potential drop between two sections equally distant from the middle and therefore at the same temperature, and the temperature at these points and at the middle. In the stationary state the Joule heating between two points is equal to the difference between the heat flowing into and out of the section. An equation is developed in which the ratio of the thermal to the electrical conductivity is expressed in terms of the voltage drop between the two points at the same temperature and their common temperature and the temperature of the middle of the bar. Meissner used a wire 0.5 mm in diameter and modified the method by using two different currents, developing an equation in which the ratio of the thermal and electrical conductivities is expressed in terms of the voltages at two points equally distant from the middle of the wire, the resistances at the mean temperatures corresponding to the two currents and the temperature coefficient of resistance. Hornbeck's data for sodium extended only over the range 0° to +90°. His values are shown on Fig. 5. These values are in good agreement with mine as to absolute values but the slope of his curve is somewhat smaller. The difference may easily be due to difference in purity or to difference in previous history. My specimen had been cooled repeatedly while his had never been cooled below 0°C. His specimen possibly was in more stable condition than mine with respect to.the change which occurs between −50° and 0°. Hornbeck did not extend his observations below 0°C and hence missed noting this change.

Meissner's values for lithium are shown also on Fig. 6. He gives values for k, .1734 at 101°, .1734 at +56°, .1730 at 0°, .197 at −182°, and .493 at −253°. We are in approximate agreement as to absolute values and as to the abnormal increase below −200°C and his data show a slight indication of the peculiar behavior between 0° and +100° but not do bring this out conclusively. His values were obtained by a rather indirect method and required besides resistance and voltage measurements an accurate measurement of the temperature coefficient of resistance. There is a marked difference in the temperature coefficient at 0° and that at 100° as shown by Fig. 7. The change in this quantity unless taken account of might easily produce the discrepancies between his values and mine in this region. In view of my many repeated observations over this range there can be no doubt as to the actual course of the line in this region.

THE WIEDEMANN-FRANZ-LORENTZ LAW

In order to test the Wiedemann-Franz law the resistance of wires of sodium and lithium was measured at the temperatures of ice, liquid

oxygen and liquid hydrogen. The wires were formed by squirting through a die and were of the following dimensions: lithium, 90 cm long, .1625 cm diameter; sodium, 51.3 cm long, .2921 cm diameter. They were wound in the form of a spiral and were measured bare. The specific resistance of the lithium at $0°$ was found to be $.885 \times 10^{-5}$, and of sodium $.426 \times 10^{-5}$. The ratio of the resistance at liquid oxygen temperature to that at $0°$ was found for both metals to be exactly that shown on the curves of Fig. 7. With the relation $\rho/\rho_0 = R/R_0$ it is therefore possible to compute specific resistances from these curves for any temperature. Table I shows for various temperatures the values of the thermal conductivity k and the electrical conductivity σ for lithium and sodium and the values of $k/\sigma T$ expressed in c.g.s. units. The Lorentz theory in its simplest form

TABLE I

Values of thermal and electrical conductivities of lithium and sodium.

$T°K$	Lithium			Sodium			
	k	σ	$k/\sigma T$ (c.g.s.)	k	σ	$k/\sigma T$ (c.g.s.)	(Hornbeck)
423	.170	7.14×10^4	23.6×10^7				
398	.169	7.57	23.6				
373	.166	8.13	23.0				
348	.161	8.70	22.4	.270	17.1×10^4	19.1×10^7	(20.7×10^7)
323	.153	9.44	21.2	.290	18.9	20.0	(20.5)
293	.149	10.35	20.6	.300	21.2	20.0	(20.6)
273	.155	11.55	20.7	.335	23.5	21.9	(21.0)
248	.163	12.85	21.5	....	.....	....	.... ..
223	.170	15.00	21.3	.280	31.4	16.9	
198	.177	17.5	21.4	.288	36.2	16.9	
173	.185	21.1	21.3	.305	43.4	17.0	
148	.192	26.9	20.2	.324	53.5	17.1	
123	.200	36.1	19.0	.340	67.0	17.3	
98	.207	57.8	15.4	.360	93.8	16.4	
73	.218	116.	10.9	.377	133.3	16.3	
33	....	.....	....	.403	226.0	22.6	
23	1.00	1050.	17.3	....	.....	....	

gives $k/\sigma = \pi/2 \ (a/e)^2 T$, where a is the Boltzmann constant, 2×10^{-16}, and e the electronic charge, 1.59×10^{-20} e.m.u. Thus at 18°C or 291°K the ratio should have the value $k/\sigma T = 24.7 \times 10^7$. The agreement shown in the tables is rather good. The steady diminution in the value of this so-called constant with lowering temperature is in agreement with more modern theory. Hornbeck developes an equation which calls for just such a falling off.

SPECIFIC HEAT OF LITHIUM AND SODIUM

The specific heat may be obtained from cooling curves on the assumption that the heat loss per cm length from rods of different material but

of the same diameter and with same surface (obtained by winding tightly with a single layer of paper) and cooling under exactly the same conditions is independent of the material of the rods and depends merely upon the temperature of the rod and that of the surrounding bath. This assumption has been thoroughly tested with rods of lead, copper and silver. With these metals, when the heat loss per com length per second, given by the expression $Ms/L \cdot dT/dt$ is plotted against rod temperatures, the points all lie on the same curve. (Fig. 2). In the cases of lithium and sodium the specific heat particularly at low temperatures were not sufficiently known to enable the computation of k. Instead of plotting the expression
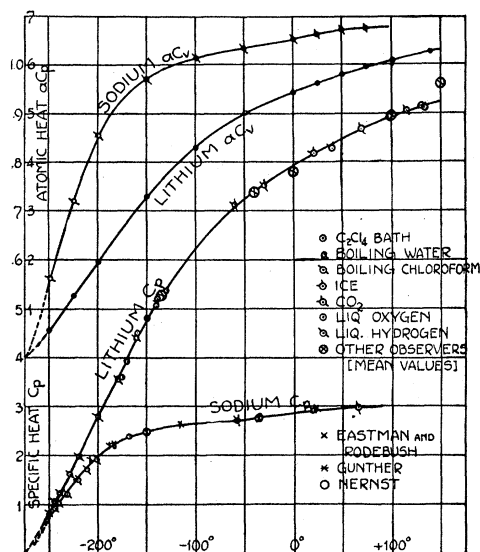

Fig. 8. Specific heat of sodium and lithium.

above for heat loss rate, the expression $ML \cdot dT/dt$ was plotted (Fig. 2). The curves lie to the right of those obtained when s is taken account of, and for any temperature the ratio of the abscissas gives the specific heat. The curves in Fig. 8 show the values of specific heats so obtained. On this plot are shown also the values obtained by other observers. The agreement for both metals is extremely good. Atomic heats aC_v are also plotted, C_v being computed by means of the Nernst-Lindemann equation[14]. For both metals the values of aC_v exceed the DuLong-Petit maximum of 5.95. The lithium values exceed this maximum above $+75°C$, the sodium values above $-125°C$. I wish to suggest

[14] Lewis, Physical Chemistry, Vol. III, 67, Longmans.

that *this excess specific heat is possibly latent heat of crystallization, i. e. heat required for the disintegration of the crystal lattice which the evidence indicates is gradually taking place.*

Debye's specific heat equation in the form $aC_v/5.95 = 77.94 \ (\theta/\theta_m)^3$ fails to fit the data for these metals. For this test θ_m was taken for lithium as 480° and for sodium at 418° on the assumption that a smooth curve expresses the relation between θ_m and atomic weight. The lithium data partially superposes the curve which has been found to be common for aluminum, copper and silver but lies above it for all the upper range. The sodium curve does not even lie near the common curve, the values of $aC_v/5.96$ being from 50% to 100% high. If the value $\theta_m = 200$ is taken for sodium the fit is about as good as for lithium.

CORNELL UNIVERSITY,
    May 1926.