

[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Thermal Conductivity of Liquid Sodium and Potassium

BY C. T. EWING, J. A. GRAND AND R. R. MILLER

Conductivity coefficients were measured for liquid sodium and potassium metals with a longitudinal heat flow apparatus—sodium to 510° and potassium to 610°. A description of an apparatus for accurate measurement of high boiling metals to 600° is presented. The ideality of the pure liquid metal media is shown by the conformation of the conductivity values to empirical and theoretical postulations.

In the application of liquid metals as high temperature heat transfer media, disagreement in conductivity coefficients was found to exist. For sodium, disagreements in the order of 40 to 100%¹⁻³ are indicative of the present state of conductivity measurements with liquid metals.

The object of the present study was to design a reliable conductivity apparatus for liquids and to measure accurately values for liquid metals to approximately 600°. A conductivity apparatus was designed for the work after careful consideration of possible error with different methods. Of the two major methods, the longitudinal heat flow type with guard tube compensation was selected over that of the Forbes bar or its modifications. The absolute heat flow in the longitudinal-type apparatus would normally be obtained for convenience from the conductivity of a known metal. However, with the accuracy desired, the uncertainty in known values for metals, particularly at elevated temperatures, made such a procedure undesirable.

In modifications of the Forbes bar method the radial heat exchange is comparable to the heat measurement in the longitudinal method. The radial exchange is calculated using either the conductivity of the insulation material or the specific heat of the liquid sample. The conductivity of insulation materials (with possible dependency on degree of packing) and the specific heats of liquids in general at elevated temperatures are not well known. The questionable quantity introduced by the use of either would normally contribute to greater error than would be expected from a careful measurement of absolute heat input. These views together with the higher probability of convection with radial heat flow in a relatively long column of liquid appeared to make any method of the Forbes bar-type unsuitable for the present studies. The criticism of the longitudinal heat flow method as advanced by Bidwell⁴ would not appear justified when proper precautions are taken for the control of radial exchange and for the absolute measurement of heat flow.

Experimental

Apparatus.—A cross-section of the center portion of the apparatus as assembled in the furnace is shown in Fig. 1. Stainless steel (type 304) was chosen as containing material and was suitably stabilized for minimum change in grain structure. The specimen bar, guard-ring, and heat sink were all machined from stainless steel to form one unit which was positioned in the furnace as shown. The machined

joint at the base of the bar permitted the bar to be interchanged as an individual unit without removal of the guard-ring.

The specimen bar at the center of the guard-ring was 1.625 inches in diameter and approximately 20 inches long. The bar proper was machined in two sections (J, F) joined by a weld (I) below the specimen chamber (H). The upper section (F) was machined with a spiral groove at the top to accommodate the platinum-rhodium sample heater (E) and was hollowed at the base to a wall thickness of $\frac{1}{32}$ of an inch for two inches to form the specimen chamber. A small hole (G) was drilled into the specimen chamber to permit filling and extended to the expansion reservoir (B) at the top. A similar heater (C) was placed above the sample heater and was to have been used, if needed, to prevent heat-flow to the top of the bar. A couple pair (T_1, T_2) was spaced between the two heaters for control and for calculation of heat-exchange with the top of the bar. Heat removal for the bar was provided in the heat sink at (L).

The guard-ring (M), which was 7 inches o.d. and 5.5 inches i.d., extended well above the top of the bar. The

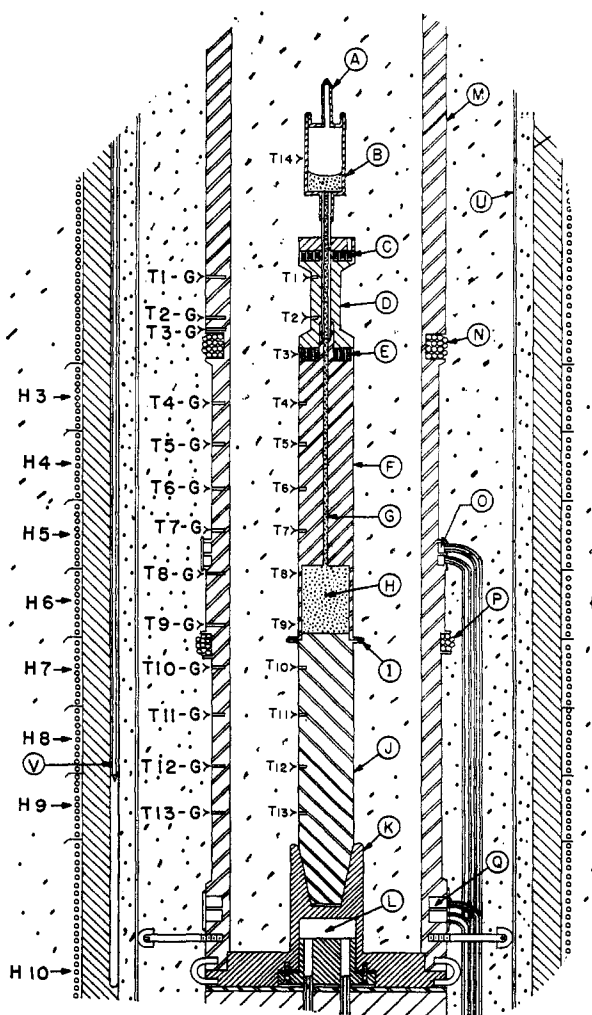


Fig. 1.—Thermal conductivity apparatus.

(1) P. A. Khalileev, *J. Exptl. Theoret. Phys. (U. S. S. R.)*, **10**, 40 (1940).

(2) W. C. Hall, *Phys. Revs.*, **53**, 1004 (1938).

(3) C. C. Bidwell, unpublished work for this Laboratory, NRL Report No. C-3152.

(4) C. C. Bidwell, *Phys. Revs.*, **56**, 594 (1939).

main guard-ring heater (N) was embedded around this tube directly opposite the sample heater. The guard-ring was provided with grooves at the base (Q), machined for equal circumferential cooling, opposite that in the bar. The conductivity of each liquid metal measured was well above that of the stainless steel. Therefore, to facilitate equalization of the gradients in the region of the liquid specimen, cooling had to be provided at (O) opposite the top of the liquid sample and heating at (P) opposite the base.

Heat removal at the desired points in the bar and guard-ring was effected with independent, dry air-flows. A cartesian manostat with surge tank, in conjunction with a controlled temperature-bath and orifice-manometers gave the required degree of control.

Temperature measurements on the sample bar were made with 5-mil. platinum, platinum-10% rhodium couples (T_4 to T_{13}). Four couples were suitably spaced in the bar above the specimen chamber and four below. The couples at the specimen chamber were peened into the steel wall. All couple leads were taken completely around the bar before being brought out, to reduce lead conduction. A 15-mil platinum couple was positioned in the guard-ring opposite each couple on the bar (T_{14} to T_{18}). Precautions were observed in the machining and assembling of each unit to assure that all couples were exactly opposite corresponding couples. Several other couples were positioned on the assembly to check temperatures at possible exchange points (T_{1G} , T_{2G} , T_{3G} , T_{14} , T_3) and T_{14G} (not shown) on the guard-ring above the conductivity bar.

All heaters on the sample bar and guard-ring were non-inductively wound, direct current heaters with power supplied from a common source, a Nobatron. Current in the individual heater circuits was regulated with parallel rheostats, mounted for uniform cooling. The absolute power input to the sample heater was measured in a shielded circuit by noting the voltage drop across the heater and that across a standard manganin resistor in series with the heater. The power to each guard-ring heater was noted with a voltmeter and ammeter of suitable ranges.

For effective control of the gradients in the guard-ring, the radial exchange between the guard-ring and the furnace had to be compensated. For this purpose, the furnace heater served as a secondary guard-ring. The nichrome heater, wound on an alundum cylinder, was divided into eleven individually controlled sections (H_1 to H_{11}) with seven sections opposite the measuring zone of the bar. Power to the furnace heaters was effectively regulated with two parallel cascades of constant voltage transformers with cascaded variable transformers in the individual circuits. Furnace temperatures were noted with moveable calibrated chromel-alumel thermocouples (V). A grounded metal shield (U) was interposed between the furnace heater and the measuring assembly.

Thermocouples and Calibration.—Of the available couple pairs only platinum-platinum rhodium offered the required stability for the conditions imposed. A Rubicon, type C, double-microvolt potentiometer with Wenner reversing key, in a completely shielded system, gave the required degree of accuracy for the measurement of the small couple voltages. The measuring system was composed entirely of copper. Precautions were observed to reduce the possibility of extraneous thermals, electrostatic charging, electromagnetic effects, current leakage to measuring system, parallel couples, etc. All terminal boxes and switch boxes were of gradient-free construction. The wiring of the switch circuit permitted that each couple could be read relative to a cold junction or relative to any one of five reference couples on the specimen bar.

The measurement of thermal conductivity is primarily concerned with the difference in temperature as related to heat-flow. The accuracy of the final result depends, from the couple standpoint, on the accuracy of the calibration of each couple relative to the others, and only reasonable accuracy need be maintained as to absolute temperature. Before the conductivity work with each metal, all couples to be used were intercalibrated against primary standard couples from the National Bureau of Standards. Intercalibrations were made at 100° intervals and were accurate to better than 0.5 of a microvolt for the temperature range.

As a check on the stability and calibration of the couples on the bar during the conductivity measurements, the design of the furnace permitted a precise intercalibration of the couples on the bar *in situ*. A small percentage of the couples

exhibited slight microvolt deviations from the original calibrations and were corrected accordingly. Obviously the small deviations could have easily resulted from strains or thermals introduced while assembling the fine couples on the apparatus. With practical elimination of thermals and stability effects, the important couples near the center of the bar were calibrated relatively to 0.3 of a microvolt.

Procedure.—The liquid metal was distilled from a nickel still onto a sintered glass filter and directly into the specimen chamber under high vacuum, and the connecting tube (A) at the top was welded closed under reduced pressure of purified nitrogen. X-Ray photographs of the specimen chamber with the metal in the solid and liquid state indicated the absence of voids. A new tube was used for each metal measured.

To measure thermal conductivity it was necessary to establish a steady heat flow in the bar and to match the temperature of each guard-ring couple to that of the corresponding couple on the bar. To make a measurement, the furnace was first heated to the desired temperature with the furnace heaters adjusted for an approximated heat flow in the bar. The bar heaters, the furnace heaters, and the air flows were then manually adjusted periodically until a steady state was reached in which the temperature at corresponding levels on the guard-ring, bar, and furnace were matched within predetermined limits. The normal gradient for a run was around 5 to 6°/cm. as measured in the stainless steel. Because of the heavy insulation of the furnace, this adjustment period required several days to attain equilibrium and eliminate the drift.

For higher precision, the thermocouple readings during a measurement were made relative to one or more couples near the center of the bar. Two or more couples were also read relative to a cold junction for the absolute temperature base. Drift of the thermocouple readings at equilibrium was negligible since identical sets of readings on the bar within the precision of the potentiometer could be obtained over a period of hours.

Thermal conductivity coefficients were calculated from the equilibrium data using the standard conduction equation with due corrections for thermal expansion and heat exchange.

Experimental Results

Conductivity coefficients for liquid sodium and potassium metals were measured—sodium to 510° and potassium to 610°. The results are plotted in Fig. 2. The values for potassium are strictly linear with temperature while those for sodium show some curvature. [The values by Hall² for sodium are plotted for comparison and show excellent agreement.] Each reported point represents a series of equilibrium experiments with the same settings over a period of hours, and in several cases days. The reported values were measured with an absolute heat source and are independent of any previous measurement except, of course, in correcting for the small radial heat flow.

Standard precautions were taken in the distillations to assure the introduction of high purity metals into the tubes. The oxide content of both sodium and potassium, based on analyses of the distilled materials at this Laboratory, is less than 0.001% oxygen. A qualitative spectrochemical analysis of distilled metal is presented below. Further contamination from the tube should not be appreciable as all external joints were heli-arc welded with an inert gas inside the tube.

Spectrochemical analysis of distilled sodium:

Ag \approx 0.0001 to 0.001%

K \approx less than 0.00001%

Li, Si, Ba, Cs, Rb, Ca, Al, Mg, Fe, Cr, Ni, Sn, Pb \approx nil

Spectrochemical analysis of distilled potassium:

Na, Ca, Al, Rb, Li \approx less than 0.00001%

Ag, Si, Mg, Cs, Ba, Fe, Cr, Ni, Sn, Pb \approx nil

Table I represents a typical equilibrium run for sodium. Couple readings are in microvolts and all have been corrected to the same standard couple. The small drift and the reproducibility of the readings on the bar over a period of hours is indicative of the control of the heating and cooling sources as well as the precision of the potentiometer measurement. In several instances, the equilibrium state for a

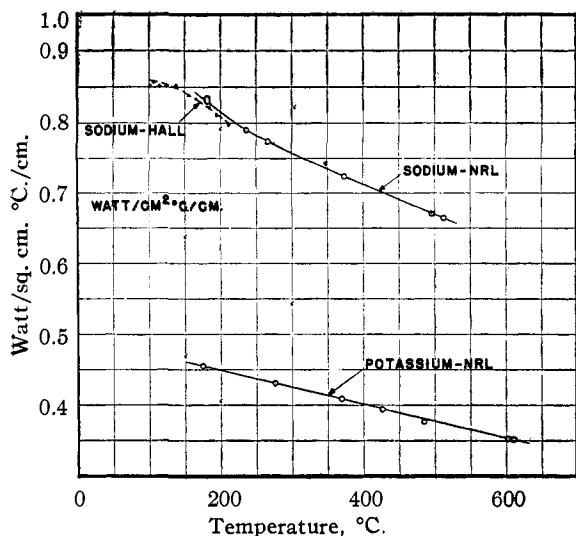


Fig. 2.—Thermal conductivity sodium and potassium.

given run was extended over a 24- or 48-hour period with no calculable change in the conductivity value.

TABLE I

TYPICAL SODIUM RUN No. 6 (374.3°)

Thermo-couple No.	Couple voltages on specimen bar in μv . (corrected to standard couple)		Couple voltages on guard-ring in μv . (corrected to standard couple)	Temp. diff. between bar and guard-ring, $^{\circ}\text{C}$.
	4: 45 P.M.	7: 15 P.M.		
1	3968.3	3968.5	4003.8 \pm 0.4	+3.6
2	3961.1	3961.3	4002.3 \pm .4	
4	3681.1	3681.3	3682.9 \pm .3	+0.2
5	3522.4	3522.6	3516.0 \pm .3	-0.6
6	3346.0	3346.2	3340.8 \pm .4	-0.5
7	3185.2	3185.4	3184.9 \pm .0	0.0
8	3040.8	3041.0	3057.0 \pm .2	+1.7
9	2974.6	2974.8	2967.2 \pm .2	-0.8
10	2832.0	2832.1	2832.2 \pm .0	0.0
11	2642.1	2642.2	2632.4 \pm .4	-0.9
12	2439.5	2439.6	2428.8 \pm .7	-1.0
13	2247.7	2247.8	2249.2 \pm .7	+0.2

The temperature gradient in the liquid metal was measured with couples peened into the stainless steel wall of the specimen chamber. To check this gradient, another gradient of somewhat lower accuracy was obtained by an extrapolation of the temperatures in the stainless steel above and below the liquid sample. For the average run the two gradients were within 0.5% of each other. The accuracy of the extrapolated gradient would necessarily be affected by the radial heat exchange. However, the close agreement of the two independent gradients is significant from several standpoints: (1) as an experimental verification of the low magnitude of radial exchange; (2) as an independent check on couple calibration, and distance measurement, as the two gradients are not related in either respect; and (3) as evidence that no void or appreciable static coefficient can exist at the liquid interfaces.

Space prohibits the complete resume of errors.⁵ However, in calculating error for the average measured result, probable random errors in the following were considered: radial exchange of heat, measurement of temperature differences, drift, measurement of dimensions, absolute measurement of heat input to the sample bar, measurement of heat exchange through (D), conductivity of the stainless wall of the specimen chamber, heat conduction along couple leads and insulation, convection and variation of conductivity with temperature.

The calculated probable error from the sources outlined

(5) NRL Report No. 3835 "The Thermal Conductivity of Sodium and Potassium."

was 1.0%. Values at a given temperature, however, were duplicated to better than 0.4%, which represents the precision of measurement.

Relative Measurement.—The apparatus also permitted a measurement of the conductivity of a liquid relative to the conductivity of the stainless steel in either the upper or lower bar. The upper bar for both the sodium and potassium tubes was taken from one end of a 15-ft. bar together with a test piece which the National Bureau of Standards consented to measure. Likewise, the lower bar for each tube was taken from the opposite end of the 15-ft. bar with another test piece. The Bureau has measured the conductivity of the two test pieces and the same materials were measured at this Laboratory in conjunction with the liquid metal measurements.

The Naval Research Laboratory measurements for the steel in the upper bars are shown in Fig. 3 and are compared with the National Bureau of Standards curve for the same material. The sodium measurement and the potassium measurement amount to two independent determinations of the same steel and show exceptional agreement. The Bureau gives a probable error of 3% for their measured curve. Actually, the agreement between the two curves is well within probable error in the range above 400°, but in the lower range probable error does not account for the differences. Similar conditions existed for the measurements of the steel in the lower bars. An attempt is being made to resolve these differences by measurements on Armco iron at the Bureau and at this Laboratory.

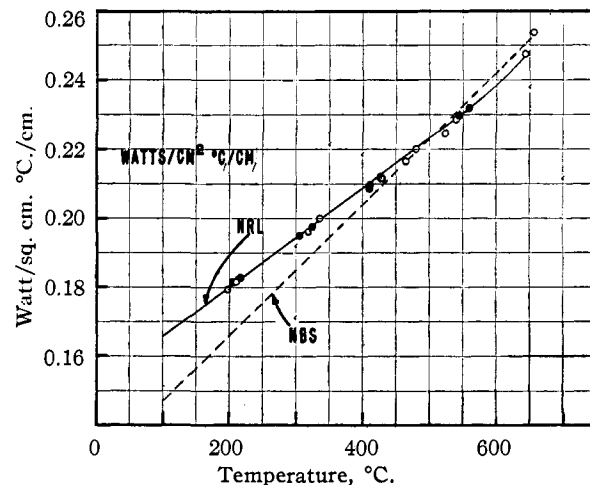


Fig. 3.—Conductivity of stainless steel (upper bar): ●, sodium measure; ○, potassium measure.

Extension of Measured Data.—The urgent need for conductivity values for the liquid metals at higher temperature made it desirable to find some method for extrapolating the measured values. Correlations in the literature have shown specific heat, density, and thermal conductivity to be interrelated.^{6,7} A relationship was developed which closely approximates the measured data for both sodium and potassium: $K/c_p d^{2/3} = \text{constant}$, where K is thermal conductivity, c_p is specific heat, and d is density.

Tables II and III show the fit of the equation to measured data for conductivity, density⁸ and specific heat⁹ for sodium and potassium. Thermal conductivity values calculated from the empirical relationship using the mean experimental constant

(6) Weber, *Ann.*, **103**, 304, 472 (1880).

(7) C. C. Bidwell, *Phys. Revs.*, **58**, 561 (1940).

(8) Naval Research Laboratory Report No. C-3287.

(9) D. C. Ginnings, T. B. Douglas, A. F. Ball, *J. Research Natl. Bur. Standards*, **48**, 23 (1950)—Sodium Data; T. B. Douglas, A. F. Ball, D. C. Ginnings, W. D. Davis, Abstracts of Papers, 119th Meeting of American Chemical Society, 48P (1951)—Potassium Data.

are listed in each table for comparison with corresponding measured values. The maximum difference between the calculated value and the measured value is 0.3% for sodium, and 1.1% for potassium, the latter occurring only at one point for potassium at 200°. The accurate fit of the experimental data to the equation should permit a reasonably accurate extrapolation of conductivity to the measured limit of specific heats—to 800° for potassium and 900° for sodium. The extrapolated values have been calculated and are listed in the tables.

TABLE II
CONDUCTIVITY EXTRAPOLATION SODIUM

Temp., °C.	Specific heat, joule/g. deg.	Density, g./cc.	Thermal cond., watt/cm. ² deg./cm. (exptl.)	$K/C_p d^{3/4}$ (exptl.)	Thermal cond., watt/cm. ² deg./cm. (calcd. by mean constant)
200	1.3393	0.903	0.815	0.721	0.816
300	1.3042	.879	.757	.720	.759
400	1.2786	.854	.712	.724	.710
500	1.2619	.829	.668	.724	.667
600	1.2548	.805			.631
700	1.2569	.780			.600
800	1.2682	.755 ^a			.573
900	1.2887	.731 ^a			.552

^a Extrapolated density.

TABLE III
CONDUCTIVITY EXTRAPOLATION POTASSIUM

Temp., °C.	Specific heat, joule/g. deg.	Density, g./cc.	Thermal cond., watt/cm. ² deg./cm. (exptl.)	$K/C_p d^{3/4}$ (exptl.)	Thermal cond., watt/cm. ² deg./cm. (calcd. by mean constant)
200	0.7899	0.795	0.449	0.833	0.454
300	.7740	.771	.424	.845	.424
400	.7642	.747	.400	.851	.397
500	.7609	.723	.376	.849	.374
600	.7638	.700	.354	.840	.356
700	.7729	.676			.340
800	.7884	.652 ^a			.326

^a Extrapolated density.

Theoretical Considerations.—It is quite possible that reliable data on the thermal conductivity of liquid metals will give greater understanding of

the structure of the liquid state. Table IV presents the results of the calculations of Lorentz' numbers for sodium and potassium using values of electrical conductivity to 350° by Borneman and Rauschenplat.¹⁰

TABLE IV
LORENTZ' NUMBERS FOR SODIUM AND POTASSIUM

Metal	Sodium			Potassium	
Temperature, °C.	100	200	350	200	350
Thermal cond. (K) watt/cm. ² deg./cm.	0.860 ^a	0.815	0.734	0.449	0.412
Electrical cond., (σ) $\times 10^{-4}$ ohm ⁻¹ cm. ⁻¹	10.36	7.59	5.42	4.59	3.19
Lorentz' number ($K/\sigma T$) $\times 10^8$ watt-ohm/(°C.)(°A.)	2.22	2.27	2.17	2.07	2.07

^a Value reported by Hall.

The value of Lorentz' number is predicted in the electronic theory of Rieche,¹¹ Drude,¹² and others. Lorentz' number, $K/\sigma T$, is theorized to be equal to $3\left(\frac{k_0}{e}\right)^2$; where k_0 is the Boltzmann constant and e is the electronic charge. Using the accepted values for the constants from "Int. Crit. Tables," the theoretical Lorentz' number is 2.23×10^{-8} watt-ohm/(°C.)(°A.).

The agreement between the calculated and theoretical values for sodium and potassium is rather good. Also, Lorentz' number for each metal shows definite indications of constancy, which is not in accord with the increase of Lorentz' number in the liquid metals as reported by Khaliilev.¹ The constancy of the values can be further analyzed when accurate electrical conductivity values are available to higher temperatures.

Acknowledgment.—The authors wish to acknowledge the helpful assistance of Dale D. Williams of this Laboratory for the preparation and analysis of the metal samples. We are also indebted to Samuel Cress and Martin B. Cavanaugh of this Laboratory for spectrochemical analysis of the metal samples

WASHINGTON, D. C.

RECEIVED JUNE 15, 1951

(10) K. Borneman and G. U. Rauschenplat, *Metallurgie*, **9**, 510 (1912).

(11) Rieche, *Ann.*, **66**, 353, 545 (1898).

(12) Drude, *ibid.*, **1**, 566 (1900).