A Precise Method of Measuring Heat Conductivity Applicable to Either Molten or Solid Metals. Thermal Conductivity of Zinc

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A metal rod or a hollow vertical graphite cylinder containing molten metal is packed in silocel contained in an outer iron cylinder. Downward heat flow is established, and vertical gradients are measured differentially by thermojunctions in quartz tubes as are also radial temperature drops across the silocel at all levels. At low temperatures the iron cylinder is surrounded by constant temperature baths, at high temperatures by additional silocel contained in magnesia pipe lagging. The differential junction measurements were obtained by raising one junction progressively while the other was left at the bottom. High temperatures were obtained by a heater winding placed directly on the specimen or graphite cylinder but insulated electrically. For either low or high temperature arrangements the gradient down the specimen is found to change with distance at a constant rate. This means that radial temperature drops across the silocel are constant from bottom to top. This was checked experimentally. Previously published values for solid zinc are verified and extended through the melting point to 730°. The drop in conductivity at the melting point agrees with data of Konno (the only data found in the literature). The values in the liquid state decrease slightly with rise of temperature. Konno's data suggested this but did not extend far enough to prove it.

INTRODUCTION

METHODS of measuring thermal conductivity by longitudinal heat flow—the only procedure possible for liquids—are unsatisfactory in several respects. Most workers have depended upon compensation of lateral or radial heat flow and assumed perfect compensation when the gradient down the rod became constant. The author has found considerable chance for judgment as to when compensation is effected and particularly a large uncertainty as to whether the source of energy producing the heat flow is the heater coil intended for that purpose or the compensating coil. Variations as high as 20 percent may result from this uncertainty. A method which avoids these uncertainties and largely eliminates the personal judgment of the observer is here reported.

THEORY OF PRESENT METHOD

The method here employed is based upon the observation that with a downward heat flow established in a test rod packed vertically in thermal insulation, the thermal gradient in the rod, under certain easily attainable conditions, changes at a constant rate as one moves down the rod and where this is true the radial heat loss across the insulation per cm length is constant. The expression which equates the radial heat loss per cm to the difference in vertical heat flow per cm is

$$2\pi k_s \Delta T/2.30 \log R_2/R_1 = k_x A d^2T/dx^2.$$

k_s is the thermal conductivity of the silocel at the temperature in question; ΔT, the radial temperature drop across the insulation (constant for all levels); R_2 and R_1, the outer and inner radii of the silocel; k_x, the thermal conductivity of the test rod; A, its cross section area; and d^2T/dx^2, the (constant) slope of gradient-distance line. Under the circumstances the insulation at its outer radius follows the same temperature drop as does the test rod although its average temperature may be 60 or more degrees lower. This was thoroughly checked experimentally. The necessary conditions can of course only be approximated[1] but *over the length at which the gradient changes are constant, the lateral losses are constant.* This is the essential idea of the method.

EXPERIMENTAL ARRANGEMENT FOR SOLID METALS

Figure 1 shows the experimental set-up as used for molten metals. For solid metals the

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[1] To attain the necessary conditions with rods 25 cm long, the top 6 cm must be disregarded. With very long rods and small heat input at the top the lateral loss toward the bottom approaches zero.

arrangement is similar except that the upper bored out part of the graphite rod is replaced by the solid metal rod. The test rod (zinc) 4 to 5 cm in diameter, 20 to 25 cm long, was mounted upon a solid graphite cylinder (heat sink) of like dimensions and centered in an iron cylinder 12 cm in diameter and 50 cm long. The space between the test rod and iron cylinder was packed with silocel. Five additional cm of silocel were packed outside the iron cylinder and contained in an outer asbestos tube. Silocel was packed above and below the specimen for about 20 cm. For low temperatures the same rods were centered in a tin cylinder, 12 cm in diameter, 50 cm long. The cylinder was closed at the bottom and the metal rod rested directly upon the tin bottom instead of on the graphite rod (sink). The top of the cylinder (above the test rod) was filled with silocel. The tin cylinder was immersed directly in constant temperature baths —cracked ice, CO_2 slush with alcohol or liquid nitrogen.

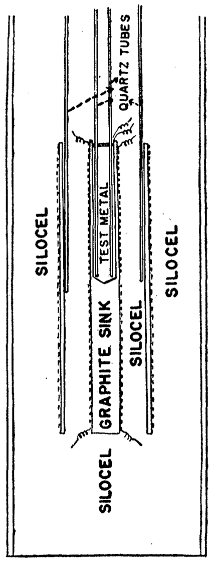

FIG. 1. Arrangement for molten metals.

Before mounting, the specimen and the graphite cylinder upon which it rested were each wound their entire length with Nichrome ribbon insulated by a single layer of asbestos paper, the winding being put on with the asbestos paper wet. Thus the specimen could be heated quickly to any desired temperature and, since the winding on the graphite was separate, any temperature gradient in the specimen could, within limits, be eliminated by adjusting the energy input into the graphite base. Alternating current was used always in these heater windings. A small pancake type heating coil was fastened to the top of the test metal, thus permitting a known input of electrical energy at the top and establishing a heat flow down the specimen. The current in this heater will be known as direct current. The specimen was originally cast with two one-eighth-inch o.d. thin-walled quartz tubes extending clear to the bottom for the insertion of thermojunctions. Temperatures and temperature gradients were measured differentially between the two junctions, one junction being raised progressively, usually 2 cm at a time, the other left at the bottom. The differential readings were read directly as galvanometer deflections. A third junction kept in melting ice could be thrown in series with either junction and the actual temperature obtained. For this latter case a potentiometer was used. Since the bore of the quartz tubes was only about 1.5 mm and since temperatures were carried as high as 800°C, the problem of insulation for the junction wires required attention. The junction wires were of Chromel and copper and it was found that heating each to a good red heat oxidized the surfaces such that no further insulation was needed. Such wires could not be twisted together as that would fracture the oxide crust but they could be laid in contact and slipped up and down the tubes with impunity.

For reading temperatures across the insulation, two quartz tubes with thermojunctions were inserted in the silocel just inside the iron or tin cylinder. These tubes extended down to the level of the bottom of the test specimen. With either of these junctions used differentially with the stationary junction at the bottom of the specimen, the temperature drop across the silocel insulation and temperature variation up and down at the outer radius of the silocel could be read.

EXPERIMENTAL PROCEDURE

The temperature is raised to the desired region by means of the heater windings on the specimen and its graphite base, with the same current in each winding. When approximate temperature equilibrium is attained (in one or two hours),

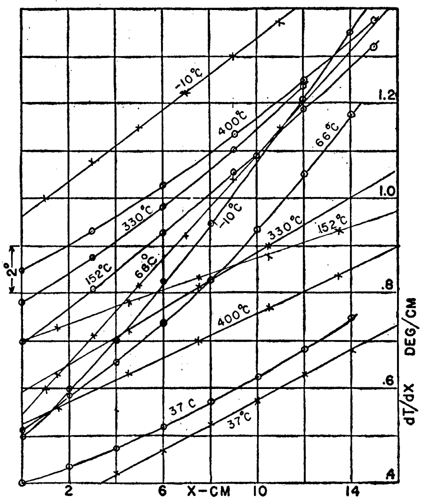

FIG. 2. Gradient data for solid zinc. T, x curves and dT/dx, x curves (straight lines).

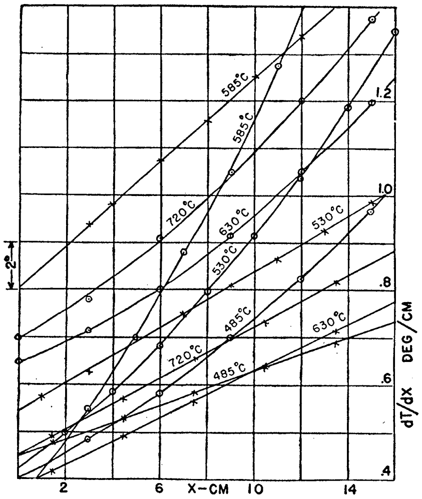

FIG. 3. Gradient data for molten zinc. T, x curves and dT/dx, x curves (straight lines).

the current in the winding on the supporting base is adjusted so as approximately to eliminate any vertical gradient in the specimen. Also at high temperatures the radial drop, ΔT, is reduced by current in a winding on the iron cylinder. After waiting again for equilibrium the residual vertical temperature gradients in the specimen and the gradients in the insulation just within the outer iron cylinder and the temperature differences across the silocel from specimen to iron cylinder at all levels are observed. Then current is sent into the d.c. heater at the top of the specimen and after approximately one hour the vertical gradients established in the specimen and those at the outer iron cylinder are read, and the radial drop across the silocel at the level of the lower fixed junctions. The radial drop at all other levels can be computed from the data. By correcting for the initial gradients, the vertical gradients down the specimen and the radial drops across the silocel *due to the heat added at the top* can be obtained. In all the above proceedings it is very necessary to continue repeating readings until they become constant.

PROCEDURE FOR MOLTEN METALS

The molten metal was contained in a graphite cylinder, 50 cm long, bored out for a depth of 25 cm, leaving walls about 4 mm thick (see Fig. 1). The lower unbored half of the graphite acted as a heat sink and contained a winding separate from that on the upper bored half. The d.c. heater consisted of a coil of Nichrome wire, B and S No. 22, wound on a $\frac{1}{8}$-inch mandril for about 3 inches and placed in a Pyrex tube. The tube was bent into the form of a circle and the ends of the tube bent upward at right angles to the plane of the circle. Thus a flat heater was obtained which was immersed in the molten metal at the top. It is always necessary that convection be eliminated by having the top slightly warmer than the bottom. This was done usually by adjusting the alternating current in the coil on the upper half of the cylinder relative to that on the lower half or by applying a small current in the d.c. heater. Temperatures and temperature gradients were measured exactly as in the case of the solid rods. In this case the two $\frac{1}{8}$-inch quartz tubes were simply lowered into the molten metal. With the molten metal one could measure the temperatures vertically up the specimen either by raising the junction in one of the quartz tubes or by raising the quartz tube itself. Careful tests gave identical results. It was more convenient to leave the tubes fixed and raise the junction.

CORRECTION FOR THE CONTAINING GRAPHITE WALLS

In determining the heat flow at the various levels down the liquid it is necessary in the case of the molten metals to estimate and correct for the flow down the walls of the graphite containing cylinder. The correction is effected by assuming the cross-section area increased by the area of the walls and *assuming the conductivity of the walls the same as that of the test metal.*[2]

Thermal Conductivity of Zinc[3]

The plotted data for solid zinc are shown in Fig. 2 and for molten zinc in Fig. 3. The curves show temperature plotted against x (distance up the rod), and the gradients (dT/dx) plotted against x. The straight lines for the latter case clearly indicate the constancy of d^2T/dx^2. Values of thermal conductivity (k) for zinc as determined from the above plots are shown in Fig. 4. The line overlaps for 100 degrees the author's previous line for zinc[4] and continues that line through change of state to 720°C in the molten condition. For comparison, data by Schofield,[5] Konno,[6] and Van Dusen and Shelton[7] are shown. Konno's points for both solid and molten zinc are in excellent agreement with those here shown. His data also agree in indicating a slight decrease in thermal conductivity with temperature for the molten metal.

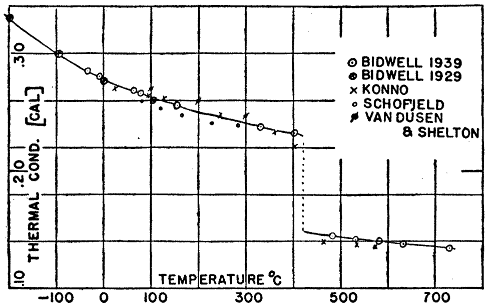

FIG. 4. Thermal conductivity of zinc.

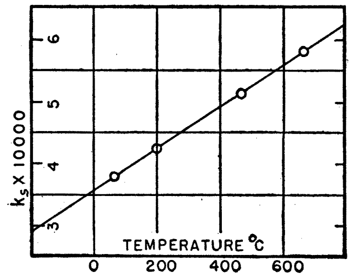

FIG. 5. Thermal conductivity of silocel.

Sample computations for k for two temperatures are shown herewith. When constant temperature baths were used the ΔT across the insulation at top (20 cm level) as observed was about 10 percent higher than at the bottom (0 level). The test rod in this case was 20 cm long and if computations are confined to the lower 14 cm, the ΔT's are sensibly the same and the equation holds. The variation in such case was not over 2 percent and the average ΔT was taken. At high temperatures, where additional silocel was used outside the iron cylinder, no variation was found in ΔT if one disregarded the top 4 cm.

Sample Data

At −37°C, $A=13.89$[8] cm², $R_2=5$ cm, $R_1=2.12$ cm, $k_s=0.000345$ cal., $d^2T/dx^2=0.050$, $\Delta T=41°$, watts input at top = 12.70. $k_x=0.285$ cal.

At 630°C, $A=15.5$, $A_{gr}=4.14$, $R_2=11.5$, $R_1=2.5$, $k_s=0.00057$, $d^2T/dx^2=0.050$, $\Delta T=58°$, watts = 30.4. $k=0.138$.

In conclusion the author ventures the opinion that the method here described is so superior to

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[2] To check this wall correction a special test was made with mercury as test material at room temperature, (1) contained in the graphite cylinder, (2) contained in a glass cylinder of approximately same internal diameter. Other conditions were as in the tests on zinc except that no heat sink was used at the bottom. 10 watts were used in the d.c. heater in each case. With the graphite cylinder, the effective cross-section area is $(A_{\mathrm{Hg}}+A_{\mathrm{gr}}-a)$, where $A_{\mathrm{Hg}}=13.84$ cm², $A_{\mathrm{gr}}=4.14$ cm², a, the correction for the cross section of the two quartz tubes, $=0.20$ cm², $R_2=6.2$ cm, $R_1=2.7$ cm, $k_s=0.00038$ cal., ΔT (observed) $=36°$, d^2T/dx^2 (observed) $=0.035$. This gives $k_{\mathrm{Hg}}=0.016$ cal. at 70°C. With the glass cylinder the heat flow down the glass is negligible compared with that flowing down the mercury and the effective cross section is $(A_{\mathrm{Hg}}-a)$, $a=0.20$, $R_2=6.2$, $R_1=2.10$, $k_s=0.00038$, ΔT (observed) $=7.5°$, $A_{\mathrm{Hg}}=13.2$, and d^2T/dx^2 (observed) $=0.075$. This gives $k_{\mathrm{Hg}}=0.016$ at 50°C. (The large ΔT observed in the first case was due to a shorter length graphite tube [24 cm of mercury as compared with 32 for glass], resulting in a small heat capacity and consequent higher temperature.)

[3] To obtain a satisfactory rod of zinc, i.e., a casting free from blow holes and "piping," the metal was melted in a graphite cylinder 5 cm in cross section, bored out to a 25-cm depth, leaving walls about 5 mm thick. This cylinder containing the melt was slowly lowered by clockwork through the furnace at the rate of about 1 inch per hour. This slow freezing from the bottom up always gave rods free from blow holes and in some cases single crystals although this report does not deal with the latter.

[4] C. C. Bidwell and E. J. Lewis, Phys. Rev. **33**, 249 (1929).

[5] F. H. Schofield, Proc. Roy. Soc. London **A107**, 206 (1925).

[6] S. Konno, Phil. Mag. **40**, 542 (1920).

[7] M. S. Van Dusen and S. M. Shelton, Nat. Bur. Stand. J. Research **12**, 429 (1934).

[8] Corrected for the area of the quartz tubes 0.20 cm.

any hitherto reported, at least where values over a wide temperature range are desired, that it should become standard.

Note on the Thermal Conductivity of Silocel

The method above described required an exact knowledge of the conductivity of the silocel insulation at all temperatures and, since this presumably depended upon the looseness of packing, a special determination was made for this material. A copper tube 4-cm o.d. and 20 cm long with an inner bore of 1-cm diameter was centered in the large iron tube above used and the intervening space packed with silocel. The iron cylinder was surrounded by about 5 cm of additional thermal insulation. A Nichrome winding on the iron cylinder allowed the cylinder and its contents to be heated to any desired temperature. A Nichrome heating coil was centered exactly in the hole drilled through the copper cylinder. This was for direct heating current. The iron cylinder was about three times the length of the copper tube, the latter centered in it and packed above and below with silocel. Thermojunctions were placed in grooves in the iron cylinder and in the walls of the copper tube. The d.c. energy input into the central third of the copper cylinder was measured as was the temperature drop across the silocel. Thus the conductivity could be determined. The silocel was tamped firmly but the degree of tamping had no observable effect on the conductivity. The value at room temperature, 0.00038, is slightly higher than the handbook value, 0.00034. The increase with temperature was found to be linear (Fig. 5).

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The Effect of High Pressure on the Order-Disorder Transformation in Alloys*

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With electrical resistance as an index of degree of order, the behavior of the order-disorder transformation under high hydrostatic pressure has been investigated with the three alloys, CuAu, Cu_3Au and CuZn. Measurements were made under pressures up to 10,000 kg/cm^2 and over the temperature range 50°C to 426°C. For temperatures below the critical point the course of the transition under pressure may be predicted from reported thermal expansion data and deductions from the Bragg-Williams' theory. The observed behavior of the alloys seems to be consistent with these predictions. Measurements made near the critical temperature with the alloys CuAu and Cu_3Au show that the critical point is raised by pressure in both cases. One alloy, alpha brass (Cu_3Zn), not hitherto included in the class of the three alloys above mentioned has been examined. The conclusion is reached that a slight ordering of the constituents of the alloy occurs under high pressure.

Introduction

The only prior work relating to this subject is apparently that of P. W. Bridgman,[1] who gave a report of the compressibilities and pressure coefficients of resistance of eighteen intermetallic compounds measured at 30°C and 75°C. Some of these compounds are capable of the order-disorder transition. The irregularity of results in all cases as compared with results for other substances was noticed and emphasized by the investigator. Sudden changes in the shape of curves, and hysteresis effects, were attributed to a shifting under pressure of the conditions of internal equilibrium, possibly to a change in the complicated type of superstructure characteristic of some of these compounds (e.g., Sn_8Cu_{31} (?) with 416 atoms in the unit cell).

If the ordering process is considered simply as a rearrangement in which atoms or ions of small diameter are fitted in the interstices between those of larger diameter so that the volume of the resulting structure is a minimum, one would expect high hydrostatic pressure to accentuate the volume differences and promote an ordered structure. With this view, the shifting of the conditions of internal equilibrium, above men-

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* Part of a dissertation presented to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

[1] P. W. Bridgman, Proc. Am. Acad. Sci. **70**, 285 (1935).