Radiant Transfer of Heat in Molten Inorganic Compounds at High Temperatures

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VARIOUS MECHANISMS by which heat is transferred in ceramics, metals, and inorganic liquids have been studied for years. As part of this study, thermal conductivities were determined for molten boric oxide and for molten "flinak" (11.5 mole % NaF, 42% KF, and 46.5% LiF) from 500° to 900° C.

Molten inorganic materials are suitable for many heat-transfer applications at high temperatures. Conductivity coefficients of boric oxide and flinak (which are typical of other inorganic liquids) represent only apparent values for specific conditions and may not be employed directly in heat-transfer calculations.

EXPERIMENTAL

Boric Oxide. Conductivity coefficients of boric oxide were measured with a radial apparatus (Figure 1). This apparatus, which accommodated the liquid sample within the annulus of two concentric, stainless test tubes, was heated to the desired temperature of measurement in a long electric furnace (not shown in Figure 1). Axial heat flow was minimized by a sectional construction of the inner stainless tube and by reserving portions of the apparatus at each end for thermal guards. Where proper precautions have been taken to avoid axial flow of heat, the thermal conductivity of the liquid sample can be obtained directly from a measurement of the heat input to the central heater and a measurement of the thermal difference across the liquid. The measured conductivities were based on that portion of the apparatus represented by the two central sections of the inner stainless tube. The four remaining sections, two at each end of the apparatus, ensured uniform radial heat flow in the measuring section.

Temperature measurements were made with four pairs of calibrated thermocouples (platinum-platinum, 10% rhodium), which were spaced 90° from each other along the measurement section. The four inner couples were inserted from the top in small holes provided in the inner wall. The couples outside the liquid sample were peened into the outer containing wall, at positions corresponding to the inner couples. A Rubicon, Type C, double-microvolt potentiometer in an effectively shielded system permitted measurement of the small couple voltages.

The properties of boric oxide are nearly ideal for the measurement of thermal conductivity in an apparatus of this type. The high viscosity and low thermal expansion of the viscous material permit the use of an unusually thick liquid layer (1.22 cm.) with no significant convection (by calculation) in the liquid layer at 900° C. To guard further against convection in the liquid, a very thin stainless cylinder was placed midway between the two measuring surfaces. Thus, the measured temperature difference included the drop across the oxide and across three thin stainless sections. With the thick liquid layer, the temperature drop across all stainless sections for an average experiment was only 1.7% of the total drop. If one takes into account questionable quantities in the thermal conductivity of the stainless steel and in the measured dimensions, error from this source (which for thin layers represents a major source of error with the radial method) is only a small fraction of 1%. The thermocouples were individually stabilized and calibrated to $\pm 0.8\ \mu$v. over the temperature range of the measurements. For the average temperature drop of 50° C. across the liquid sample, uncertainties in the temperature measurement introduced an average error to the final result of less than $\pm 0.5\%$. When all other known sources of error are considered (including axial flow of heat, positioning of central heater, and dimensioning), the apparent thermal conductivities of boric oxide were measured with a probable error of $\pm 2.0\%$.

The apparatus was filled by adding solid boric oxide to the outer test tube (with the center section removed) and heating the material at 600° C. for 30 hours. The center section was then carefully inserted and welded into place. This preheating procedure was required to remove all bubbles from the viscous melt.

Apparent conductivity coefficients for boric oxide are presented in Figure 2; three distinct sets of data are shown. The lower curve represents the initial results, which were reproducible up and down the temperature scale between the limits of 500° and 800° C. However, after the apparatus was heated at 950° C. for 2 days, a similarly reproducible

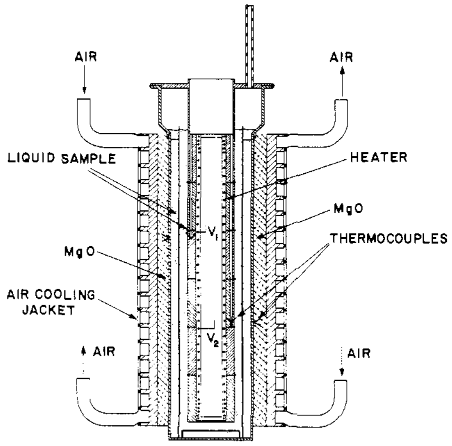

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Figure 1. This sectional view shows the detailed construction of the radial heat transfer apparatus for boric oxide

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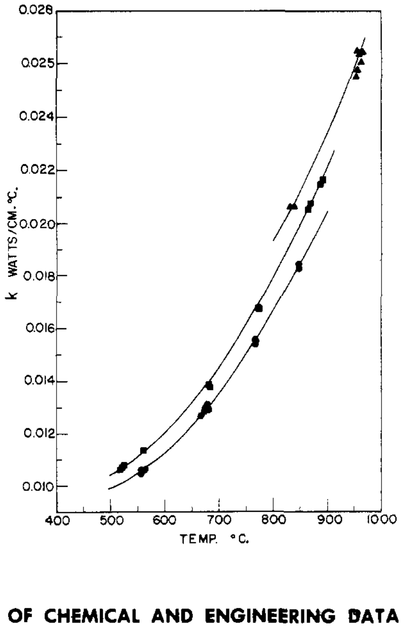
Figure 2. In the thermal conductivity of boric oxide against temperature, three curves are presented which show increasing values as the container wall emissivity increased



set of values was obtained which gave a somewhat higher curve. The apparatus was then heated to 950° C. for 11 days, and the results on the third and still higher curve were measured after this long heating period. At the conclusion of the measurements, the stainless surfaces in contact with boric oxide were found to be dark black or green, while the bulk boric oxide was transparent and clear. Based on the visual evidence of the near black surfaces and on additional experiments discussed later in this article, the shift in the measured results has been attributed to the increasing emissivity of the stainless surfaces due to reaction with the oxide at temperatures in excess of 900° C.

Flinak. The uniaxial apparatus for measuring flinak is shown in Figure 3. The method and control systems were similar to those illustrated and described in preceding work on liquid metals (*2*, *3*). The conductivity measurements were made on a centrally located, Inconel bar, which contained the liquid salt in a chamber at the middle of the bar. This bar was 1.97 inches in diameter above and below the chamber, which was 1 inch long and 1.62 inches i.d. with a wall thickness of 40 mils. The specimen bar was compensated to prevent radial heat exchange by the surrounding, thick, metal guard ring (7 o.d. and 5.5 inches i.d.). Thermal gradients within the bar and compensating gradients in the guard ring were established by direct current heaters at the top of each and by uniform air cooling at the base of each. To compensate in the guard ring for the large thermal drop in the salt, auxiliary heating was supplied on the guard ring at a point opposite the top of the liquid chamber and auxiliary cooling at a point opposite the bottom of the chamber. Thermal gradients were measured and controlled with 30 individually calibrated thermocouples of platinum–platinum, 10% rhodium (*2*) suitably positioned at known levels on the bar and guard ring. The entire apparatus, bar and guard ring, was maintained at temperature for measurement by a large electric furnace with 11 uniformly wound elements, which also provided a secondary thermal guard.

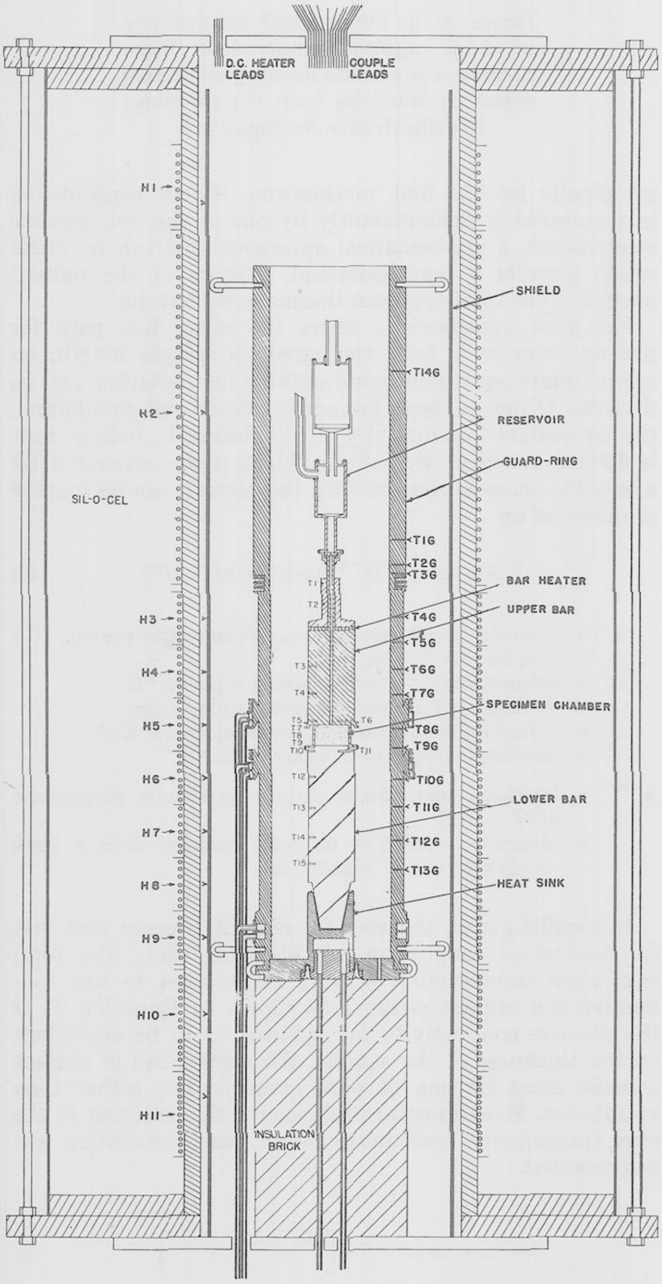


Figure 3. This sectional view shows the detailed construction of the uniaxial thermal conductivity apparatus

Since the thermal conductance of the Inconel was about six times that of the liquid salt, approximately 40% of the total heat flow at the specimen chamber passed through the Inconel wall. To provide the large heat flow required by the wall, without causing convective currents in the liquid, the top and bottom bars were made larger in diameter than the specimen chamber. The excess area at the top was designed to deliver the majority of the heat required by the chamber wall; and, similarly, the excess area at the bottom was designed to remove wall heat. This arrangement minimized radial flow of heat through the salt and Inconel at the top and bottom of the chamber.

To ascertain the extent of radial heat flow at the solid-liquid interfaces, it was necessary to install a source of heat and to provide a method of measuring temperatures near the interfaces. To supply excess heat to the chamber wall, an auxiliary circumferential heater was installed immediately adjacent to the top of the specimen chamber. Two thermocouples at each interface, one near the center of the bar and one near the edge, were installed to indicate the radial temperature difference in the Inconel.

The conductivity work with the salt was complicated by small temperature differences observed at each liquid-solid interface when heat was flowing. Initially, it was not known whether the temperature drops represented true interface resistance or were merely apparent resistances created by poor distribution of heat between the wall and the salt. Therefore, several experiments were made with an addition of heat (with the circumferential heater) at the top of the specimen-chamber wall to test the relative distribution of heat between the wall and salt. Temperature gradients across the salt at the center of the bar were measured with the central couples at the solid-liquid interfaces and compared to corresponding gradients measured along the containing wall. The ratio of the temperature gradient at the center of the bar to that in the wall was found to be independent of the additional heat added at the wall. If poor distribution of heat had existed, the addition of heat near the top of the wall should have introduced proportionately more heat into the wall than into the salt. It was concluded that the temperature drops observed at both interfaces represented true interface resistances.

The temperature gradients in the salt were measured with thermocouples peened into the wall of the specimen chamber. If these gradients had been measured with the couples inserted in the Inconel bar at the interfaces, an error would have been introduced by the drop in temperature at each interface. The combined temperature drop at both interfaces was significant and represented approximately 7% of the total temperature drop in the salt.

The sample of salt used for the conductivity studies was evacuated in a chamber above the reservoir (Figure 3) at 400° C. for 48 hours before being introduced to the reservoir and the specimen chamber. The bar was then operated throughout the measurements as a closed system under argon. An analysis of the salt, prior to the conductivity experiments, showed a total impurity content of 0.13% (by weight as metals) which was distributed as follows: 0.055% Fe, 0.012% Al, 0.009% Ni, 0.014% Pb, 0.010% Mn, 0.008% Mg, and 0.002% for several other metals. Another analysis, made at the completion of the measurements, showed little change in the above metals, but chromium was now present to the extent of 0.12%.

The apparent thermal conductivities of flinak from 500° to 850° C. are shown in Figure 4. Each result is based on an equilibrium run covering a period of 2 to 3 days. The results can be represented by three curves, indicating a downward shift in conductivity with time. Each shift to a new conductivity curve was associated with a preceding high temperature heating of the salt. After each apparent drop the conductivities were reproducible along the new curve. At the termination of the measurements the salt was noticeably colored, presumably because of the solution of chromium; and the metal surfaces in previous contact with the salt were very dark. Based on this visual evidence and on the radiant mechanism for heat transfer which is to be presented, the shift in conductivity coefficients has been attributed to a decrease in radiant transmission through the material due to the solution of an absorbing impurity.

Since 40% of the total heat flow from the sample bar passed through the metal wall of the chamber, it was necessary to have accurate thermal conductivities of this Inconel to use in correcting the salt data. Therefore, the conductivity of the Inconel bar was determined from 500° to 900° C. in conjunction with the salt measurements. The thermal conductivities for Inconel agree closely with those reported by several investigators (*4, 6, 7*) and are

T^a	C^b	T^a	C^b	T^a	C^b
545	0.210	639	0.242	736	0.262
568	0.228	668	0.248	774	0.268
574	0.218	686	0.252	799	0.273
625	0.233	688	0.256	810	0.273
625	0.238	697	0.255	876	0.276

[a] T = temperature, ° C. [b] C = conductivity, watts/cm., ° C.

THEORETICAL CONSIDERATIONS

For a liquid exhibiting radiant transmission of heat with no electronic transfer, the effective thermal conductivity may be considered to be composed of two parts—one due to molecular conduction and the other to radiant transfer. According to classical theory (*8*), the molecular conductivity, k_m, can be expressed by Equation 1. For amorphous materials, such as the fused inorganics, the atomic disorder should determine a mean free path, l, which is practically constant with temperature. Likewise, c and v are known to be roughly constant for most fluids over reasonable temperature ranges. This classical theory is presented only to show that the molecular conductivity for an inorganic liquid should be reasonably constant for temperatures above the Debye temperature.

$$k_m = cvl/4 \tag{1}$$

c = specific heat at constant volume
v = velocity of heat waves
l = mean free path of the waves

The mathematical treatment of radiant transfer within a material is complex (*1, 5*) and can be solved only for the simplest cases. Two mechanisms of radiant transfer have been identified (*5*). The first is by transmission directly through the material and follows the normal absorption laws for light. The second is by transmission, absorption, and reradiation within the body of the material. For a short section of any material which transmits strongly in the infrared, transfer of radiant energy should occur principally by the first mechanism. Where transmission in a material is predominantly by one of the two possible mechanisms, a mathematical approximation can be made which permits a semitheoretical analysis of the radiant portion of the total apparent thermal conductivity.

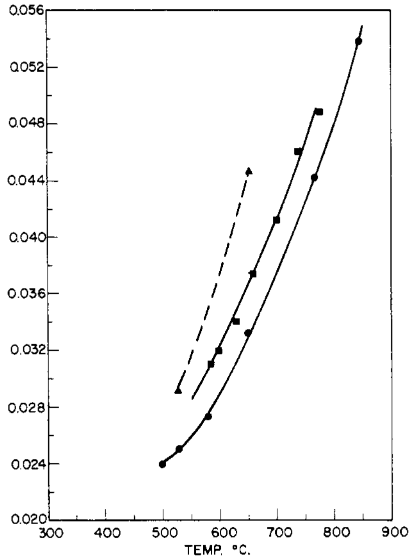


Figure 4. In the thermal conductivity of flinak against temperature, three curves are presented showing decreasing values as impurties from the container are dissolved in the liquid salt

For pure transmission, where the mean free path for photon transfer is long compared to sample length, an approximate equivalent conductivity for radiation can be derived. If one neglects boundary effects and reradiation, the equivalent conductivity for radiation k_r (where heat is flowing between two infinite, black plates separated by a liquid in thermal contact with the plates), can be roughly represented by

$$k_r A\Delta t/\Delta x = A\ (e^{-\alpha\Delta x})\ \sigma\left[(T+\Delta t)^4 - T^4\right] \tag{2}$$

k_r = equivalent conductivity for radiation (watts/per cm., ° C.)
A = area for heat flow, sq. cm.
Δt = temperature difference between the plates, ° C.
Δx = thickness of the liquid between the plates, cm.
σ = Stefan-Boltzman constant, watts/sq. cm., (° K.)^4
T = absolute temperature of cooler plate, ° K.
$e^{-\alpha\Delta x}$ = fractional transmission at average sample temperature of $(T + \Delta t/2)$
α = absorption coefficient for total emission from a black body source at $(T + \Delta t/2)$, cm.$^{-1}$

In parallel plates, the area for radiant transfer and that for equivalent conduction are identical; thus, the total equivalent conductivity, k, may be equated to the conductive and radiant portions as shown in Equation 3. If the effective conductivity for radiation is to be dependent on the thickness of the sample, the mechanism of radiant transfer must be one of pure transmission, rather than reradiation. Experimental evidence for the selection of the pure transmission mechanism rather than reradiation will be presented.

$$k = k_m + \Delta x\ (e^{-\alpha\Delta x})\ \sigma\left[\frac{(T+\Delta t)^4 - T^4}{\Delta t}\right] \tag{3}$$

The transmission to be expected through samples of boric oxide and flinak cannot be calculated, since absorption coefficients are not available. However, the transmission through each material can be approximated from an analysis of the measured conductivities. For this purpose, Equation 3 has been reduced to the simpler form shown in Equation 4 where, for convenience, ($e^{-\alpha\Delta x}$) has been replaced by an equivalent transmission coefficient, C_t; and a factor, F, has been added for the usual gray radiating surfaces. This factor incorporates the emissivities of the radiating surfaces and other boundary effects. In the application of Equation 4, if as a first approximation the molecular conductivity and the transmission coefficient are constant with temperature, the total apparent conductivities should be a linear function of

$$\sigma\left[\frac{(T+\Delta t)^4 - T^4}{\Delta t}\right]$$

for a particular system.

$$k = k_m + F\,\Delta x\,C_t\,\sigma\left[\frac{(T+\Delta t)^4 - T^4}{\Delta t}\right] \tag{4}$$

ANALYSIS OF RESULTS

Boric Oxide. The apparent conductivities for boric oxide were measured in a radial apparatus in which the areas for radiant transfer and equivalent conduction are not identical. However, if a small correction term, (A_r/A_c), is added to Equation 4, the heat flow in the radial apparatus can be treated as a flow between two infinite plates. A_r is the area for radiation, and A_c is the area for equivalent conduction. The conductivity data can then be analyzed for radiant contribution by the conformance of the data to Equation 4.

For boric oxide three reproducible sets of data for thermal conductivity were obtained. In Figure 5 the apparent conductivity coefficients for each set are shown to be a linear function of $\sigma\,(A_r/A_c)\left[\frac{(T+\Delta t)^4 - T^4}{\Delta t}\right]$
The slope of each curve should be approximately equal to ($\Delta x C_t$) for black radiating surfaces, and the intercept should represent the molecular conductivity. If the surfaces are gray rather than black, the slope of each curve will then represent the product, ($F\,\Delta x C_t$), where F is an emissivity factor based primarily on the emissivities of the radiating surfaces. In the radial apparatus one metal shield was interposed between the two primary radiating surfaces, and under this condition the slope obtained using this apparatus should be equal to ($F\,\Delta x C_t$)/2.

The slope of each curve in Figure 5 is believed to represent ($F\,\Delta x C_t$)2 for the condition of the surfaces during each set of measurements. The upper curve is based on the final measurements with boric oxide (the surfaces being visually black at the conclusion of the measurements) and should be most representative of heat transfer with black-body radiating surfaces. From the slope of this curve, with a liquid thickness of 1.23 cm., the transmission coefficient, C_t, for boric oxide is unity for a chosen surface emissivity of 0.95 (F = 0.90), and is 0.90 for a surface emissivity of unity. In any event, the transmission coefficient for boric oxide ranges between 0.90 and unity. An emissivity factor based on a selected emissivity for clean stainless surfaces would predict a slope in the range of that shown by the lower curve in Figure 5, which is representative of the heat transfer before surface reaction. The intercepts for all three curves were nearly the same and gave a value of 0.0054 watt/cm., ° C., for the molecular conductivity.

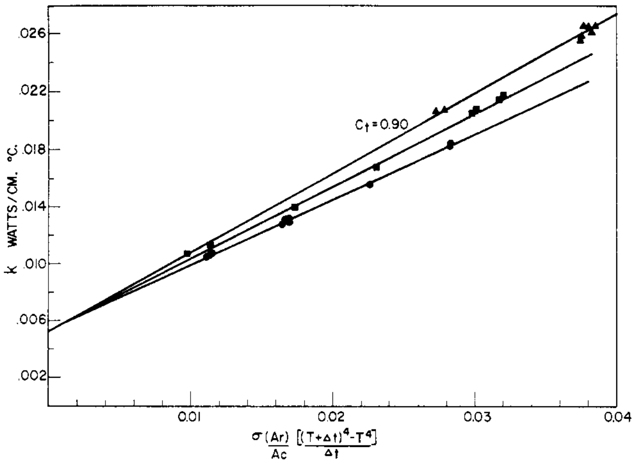


Figure 5. In the radiant transfer of heat in boric oxide liquid in the radial apparatus, three sets of data are presented showing increased transmission coefficients as the container surface emissivity changes

The conductivity results from the radial apparatus were analyzed on the premise that all radiant transfer is by pure transmission, and that the effective conductivity for radiation is effectively proportional to the thickness of the liquid layer. To identify further the mechanism of transmission, additional conductivity measurements of lower precision were made using a longitudinal system and a liquid thickness of 5.3 cm. The apparatus consisted essentially of two stainless bars, each 1⅝ inches in diameter separated by a 5.3-cm. layer of liquid boric oxide contained within a thin stainless wall. Apparent conductivity measurements were made relative to the stainless bars, which were calibrated standards from previous work (*3*). Calibrated platinum-platinum, 10% rhodium thermocouples were installed at known distances on both the upper and lower bar, so that the heat flow into and away from the liquid layer could be calculated. The longitudinal apparatus was surrounded by a sectional furnace which was used as a guard to minimize radial exchange of heat. The unusually high viscosity of the oxide permitted the use of a thick layer without inducing a major convection error.

If one neglects the influence of wall on the radiant transmission, the flow of heat in this longitudinal apparatus is comparable to the flow of heat between two parallel plates separated by a 5.3-cm. layer of liquid. The metal radiating surfaces in this case were preheated at a high temperature, and the initial surfaces were assumed to be black. In Figure 6 the apparent conductivity coefficients for boric oxide from this second apparatus are plotted as a function of

$$\sigma\left[\frac{(T+\Delta t)^4 - T^4}{\Delta t}\right]$$

Although the conductivity coefficients are many times higher than comparable values in the previous apparatus, the coefficients are again linear with the fourth-power term. The intercept again predicts a value of 0.005 watt/cm., ° C., for the molecular conductivity. The slope of the curve for a liquid thickness of 5.3 cm. predicts a transmission coefficient of 0.98.

For boric oxide the equivalent conductivity for radiation in this apparatus was about nine times higher than comparable values in the radial apparatus. Since the effective liquid thickness in the radial apparatus with the single shield was 0.61 cm., the equivalent conductivity for radiation does vary directly with the thickness of the liquid layer.

Flinak. The flinak data also resulted in three reproducible conductivity-temperature curves. A downward shift in results was shown to occur after each high temperature heating of the salt and was attributed to reaction of the material with its container. If wall influence is neglected, heat flow in the uni-axial apparatus used can be treated

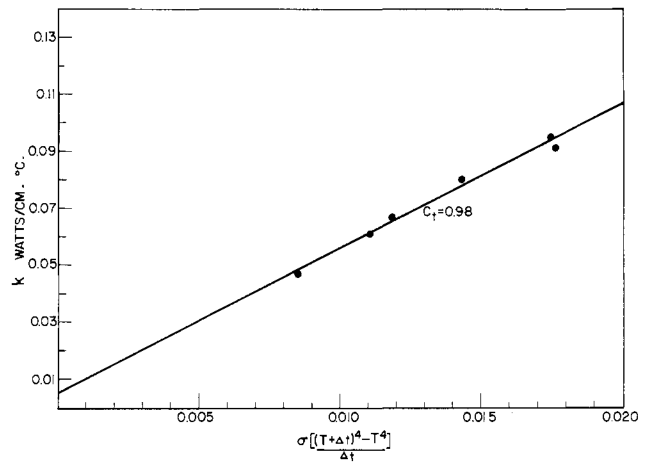


Figure 6. The radiant transfer of heat in boric oxide liquid in the longitudinal apparatus is shown where surface emissivity does not change

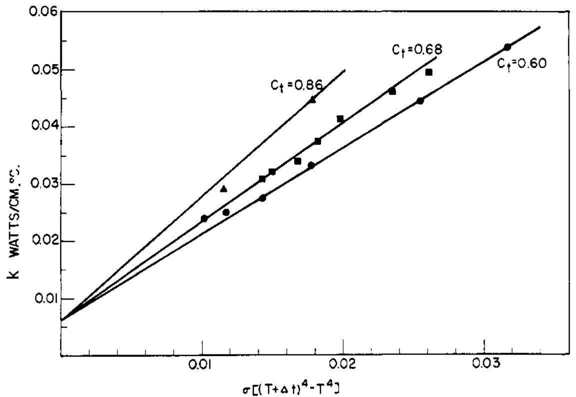


Figure 7. The radiant heat transfer in flinak is presented by three sets of data which show decreasing transmission coefficients due to solution of container components

as the flow between two parallel plates separated by a 2.54-cm. layer of the liquid. Thus, the data for the salt mixture can be analyzed directly for radiant contribution by the fit obtained to Equation 4.

The apparent conductivity coefficients for flinak are plotted as a function of the fourth-power term in Figure 7. The two lower curves represent the results after successive high temperature heatings of the salt and show a linear conformance of conductivity to the fourth-power term. The upper curve has been represented as linear, and is based on the initial measurements with the salt which are believed to be representative of the material before solution of container metals. Surfaces heated in contact with the salt mixture were visibly dark. If the experimental surfaces are assumed to be black; the slope of each curve will represent the product, ($\Delta x C_t$), for the condition of the salt during each set of measurements, and the intercept will represent the apparent molecular conductivity. The intercepts for all curves are the same and give a value of 0.006 watt/cm., ° C., for the molecular conductivity. With a liquid thickness of 2.54 cm., the transmission coefficient for the top curve (representing the liquid salt before solution of container metals) is 0.86. As the salt progressively reacted with or dissolved the container, the adsorption coefficients undoubtedly increased and the transmission coefficient dropped to 0.68, then to 0.60 for the lower curve, and would probably have dropped still lower upon further reaction. The assumption of an emissivity lower than 0.92 for the initial Inconel surfaces would give an initial transmission coefficient greater than unity.

DISCUSSION

Although the evidence presented in this article is not conclusive, it does indicate that the applicable absorption coefficients for both boric oxide and flinak are low and that radiant transmission through short sections of either pure material approaches 100%. For boric oxide two apparatus were used to show that the equivalent thermal conductivity for radiation varies directly with the thickness of the liquid layer. This direct proportionality can exist only where the fractional transmission $e^{-\alpha\Delta x}$ through a material approximates unity, and with boric oxide it does point to a mechanism of pure transmission. The other possible mechanism or contributing mechanism might have been one of transmission, absorption, and reradiation. However, for the latter type of transmission, the apparent conductivity should be less dependent on liquid thickness, and the transmission coefficient should be only a fraction of the near unity value found.

The present work provides strong evidence that the heat flow between infinite surfaces, separated by either of the liquid materials studied, may be represented by Equation 5. Surfaces which have been heated in contact with either material at elevated temperatures are shown to be effectively black, because of surface reaction (F = 1). In all practical applications, both static and dynamic, where heat is flowing across a material of this type, calculations must make proper allowance for both conduction and radiation.

$$q/A = k_m\,(T_2 - T_1)/\Delta x + F\,C_t\,\sigma\,(T_2^4 - T_1^4) \qquad (5)$$

q = rate of heat flow
T_2 = absolute temperature of the hotter plate
T_1 = absolute temperature of the cooler plate

The application of Equation 5, or modifications, to practical heat-transfer problems (where surface emissivities are known), requires only a knowledge of the molecular conductivity and the transmission coefficient. The effective molecular conductivity of boric oxide has been shown to be approximately 0.0054 watt/cm., ° C., and that of flinak to be approximately 0.006 watt/cm., ° C. Based on the present work, transmission coefficients for both materials (for thicknesses less than 2 inches) will initially be near unity. For flinak, where solution of container materials resulted in increased absorption, the transmission coefficients were reduced to a value of 0.5. The dependence of the transmission coefficient on liquid thickness, $C_t = e^{\alpha\Delta x}$, cannot be neglected for higher absorption coefficient. The transmission coefficient for boric oxide was not influenced by its stainless container. However, molecular conductivity would be expected to become predominant for either liquid when contaminated by absorbing materials.

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