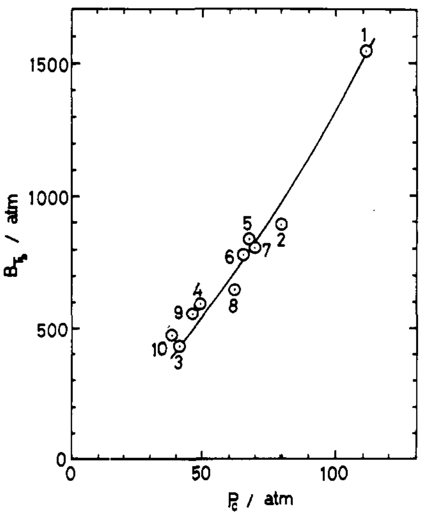

Figure 2. Tait parameter B_{T_b} at boiling point vs. critical pressure. (Numbers refer to compounds in Table III.)

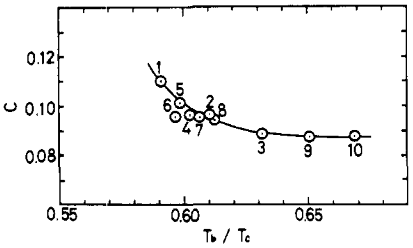

Figure 3. Tait parameter C vs. ratio T_b/T_c. (Numbers refer to compounds in Table III.)

from the curve presented in Figure 2, and were compared with the literature values. The result of this comparison is presented in Table III, in which the percentage deviation is defined by $100(V_{\text{exptl}} - V_{\text{calcd}})/V_{\text{exptl}}$. The specific volumes calculated by eq 1 by using the generalized eq 4 and C obtained from Figure 3 reproduce the literature data within 1.4%.

Glossary

B_T, C	Tait equation parameters, atm and dimensionless, respectively
P	pressure, atm
T	temperature, K
V	specific volume, cm^3/g

Subscripts

b	normal boiling point
c	critical point
0	reference state

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Thermal Conductivities of Trialkyl Borates[†]

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This paper reports the thermal conductivities of the following trialkyl borate homologues as functions of temperature: methyl, ethyl, propyl, isopropyl, butyl, and isobutyl. A concentric sphere apparatus was used for the measurements. The close agreement between observed and reported literature values for benzene seemed to justify the use of this apparatus for the measurement of thermal conductivities.

This paper is the latest in the series of papers dealing with the systematic measurements of physicochemical properties of several homologous trialkyl borates. The previous studies have reported data on vapor pressures (*2*), densities and absolute viscosities (*3*), surface tensions (*4*), and refractive indices (*5*) as functions of temperature up to the normal boiling point. The object of the present investigation has been to measure the thermal conductivities of the following trialkyl borates over the same range of temperatures: methyl, ethyl, propyl, isopropyl, butyl, and isobutyl. A review of literature has revealed no information with regard to the thermal conductivities of these compounds. This, coupled with the importance of this property in the design of heat exchange equipment involving these compounds, has provided the impetus to undertake this work.

Apparatus

The defining equation for thermal conductivity is the Fourier law of conduction, which can be stated as

$$q = -kA\frac{dT}{dr} \qquad (1)$$

where q = rate of heat flow by conduction (J/s), k = thermal conductivity, (J/(m s K)), A = area normal to the direction of heat flow (m^2), T = temperature (K), and r = radial distance over which heat flows by conduction (m).

[†] This work was abstracted from the M. Eng. thesis of L.D.T., University of Louisville, Louisville, KY, 1978.

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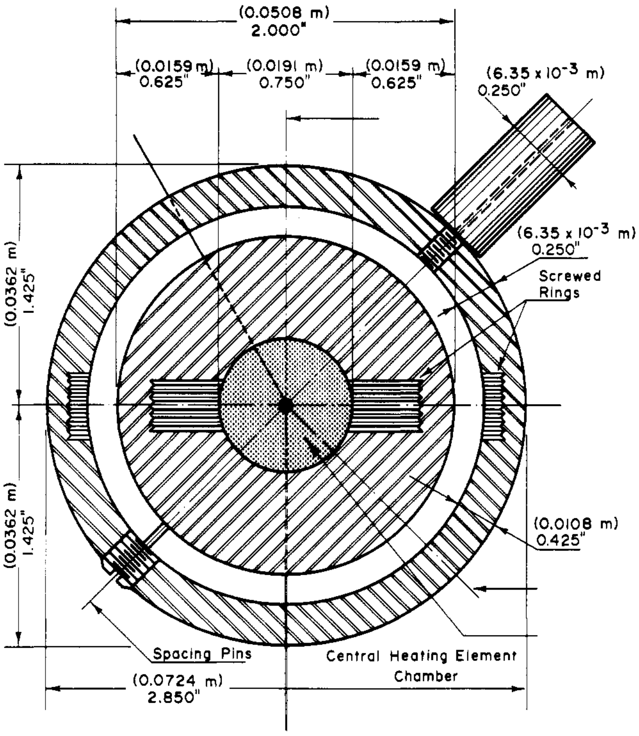
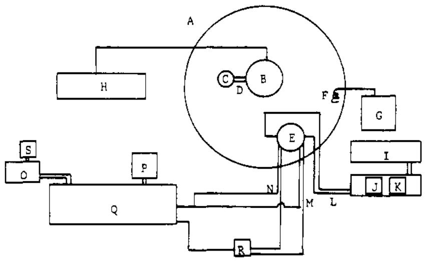


Figure 1. Concentric sphere thermal conductivity cell.



Schematic Key

A	Constant Temperature Bath	K	Ammeter
B	Heater-Stirrer Assembly	L	Power Leads to Central Heating Element
C	Bimetallic Thermoregulator	M	External Thermocouple Wire
D	Temperature Control Wiring	N	Internal Thermocouple Wire
E	Thermal Conductivity Cell	O	External Galvanometer
F	Cooling Coil	P	External Standard Cell
G	Portable Cooling Unit	Q	Potentiometer
H	Thermo-Controller Assembly	R	Toggle Switch
I	12-Volt DC Regulated Power Supply	S	6-Volt AC Regulated Power Supply
J	Voltmeter		

Figure 2. Schematic diagram of equipment.

To use eq 1 for the determination of the thermal conductivity of a sample, we provided a known quantity of heat to the sample and the resulting temperature gradient was measured. The cross-sectional area, A, and distance, r, were determined by the geometry of the apparatus.

The apparatus used in this investigation (*1*, *10*, *11*) consists of two concentric spheres made of 304 stainless steel with a heat source located at the center of the inner sphere; the test liquid is contained in the annular space between the two spheres. A dimensioned drawing of this thermal conductivity cell is shown in Figure 1. Each sphere consists of two hemispheres which can be joined by an outside-threaded internal ring. Several pins tetrahedrally located in the wall of the outer sphere maintain constant spacing and concentricity between the spheres. In the center of one of the larger hemispheres an additional opening is provided for charging and emptying the annular space; a threaded 304 stainless steel rod fits this opening. This rod is used to suspend the cell in a bath that will be described later. In the outer sphere three additional openings exist. One of these provides entry for a thermocouple, while the other two are used for electrical leads to the central heating chamber; they consist of 0.05-in. (0.001 27 m) diameter zirconium wire (this material was used because of its low thermal resistivity). The inner sphere contains two openings of the same size which provide access to these leads. The central heating element is a 39-Ω, 0.5-W resistor. This resistor is surrounded by a packing made of carbon black and epoxy resin which fills the core of the inner sphere.

A schematic of the experimental assembly is shown in Figure 2. The equipment consists of the thermal conductivity cell, heat generation equipment, a constant-temperature bath, temperature measuring system, and cell evacuation system. The electrical heat generation system consists of a regulated, 12-V dc power supply, a variable resistor, a Weston voltmeter and ammeter, and the central heating element. The power to the central heating element is controlled by a variable resistor, and from the amperages and voltages indicated on the meter the rate of heat generation by the central heating element can be calculated.

The constant-temperature bath, in which the cell is immersed during experimentation, is a 7-gallon glass bath equipped with a controllable heater-stirrer and a cooling coil which is operated by means of a portable cooler. The heater and cooler provide the capability of measurements over a wide range of temperatures. The bath is equipped with a Beckmann thermometer which maintains bath temperature readings to within ±0.01 °C. The bath heat transfer medium is a stabilized light mineral oil, which is constantly mixed by a stirring mechanism.

The cell temperature measurement system consists of two copper–constantan thermocouples. One thermocouple is soldered to the external surface of the inner sphere while the other is attached to the outside surface of the outer sphere with epoxy cement. The latter location allows for easy inspection and repairs. This arrangement results in a higher observed temperature drop by an amount equal to that through the outer metal wall. However, the temperature drop can be calculated and used to correct the measured temperature drop. The thermocouple emf's are measured by a Rubicon Type B potentiometer.

The cell evacuation system consists of a Gast vacuum pump and a fitting designed for the threaded opening in the outer sphere. Also needed is a cylinder of dry nitrogen which is used to flood the cell before filling with the sample liquid. This is necessary because all the borates are hygroscopic and therefore have to be kept out of contact with air.

Experimental Procedure

The borates were assayed and purified in the manner described previously (*2*).

The presence of the zirconium leads and the tetrahedral pins necessitates that the conduction heat loss through these elements be calculated and subtracted from the observed conduction heat transfer rate for the cell containing the sample so as to arrive at q for use in eq 1. To get an estimate of this loss, we assembled the cell and epoxy resin was applied to the openings in the outer sphere. The apparatus was then immersed in the constant-temperature bath and allowed to reach thermal equilibrium. Then, by use of the vacuum pump, the cell was evacuated to the maximum capacity of the pump, 5.5 mmHg, or 667 Pa. Next, the power supply for the central heating element was turned on. Thermocouple emf's were monitored every 5 min, and two identical consecutive readings were taken as an indication of thermal steady state. At the equilibrium point, the temperature difference across the evacuated annulus, the amperage, and the voltage of the heat source were recorded. Twelve runs at various bath temperatures and power inputs showed negligible changes in the cell heat loss.

To determine the thermal conductivity of benzene, which was used as a standard, and to thereby ascertain the ability of the concentric-sphere apparatus to measure a known conductivity correctly, we charged the annulus with 41.5 mL of benzene by

Table I. Cell Heat Conduction Losses

volts	amps × 10^2	fluid ΔT, mV	bath temp, K	heat loss, W/μV × 10^3
1.93	4.3	40	318.05	2.07
2.40	5.6	68	318.05	1.98
2.40	5.6	65	318.05	2.07
2.81	6.0	86	318.05	1.96
3.00	6.6	98	318.05	2.02
3.65	8.0	151	318.05	1.93
1.93	4.3	41	340.95	2.02
1.93	4.2	41	340.95	1.98
2.40	5.3	66	340.95	1.93
3.00	7.0	102	340.95	2.06
2.40	5.3	63	365.95	1.98
3.42	8.0	133	365.95	2.06

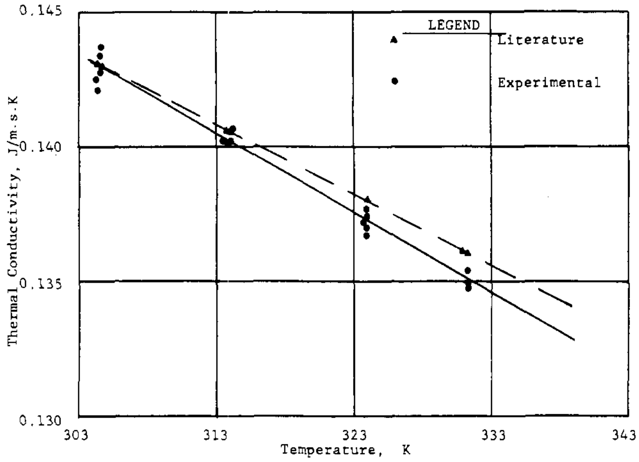


Figure 3. Thermal conductivity temperature dependence for benzene.

means of a 100-mL hypodermic syringe. After the cell was charged, it was allowed to set for 5 min to allow any air bubbles to rise. Any additional benzene needed to completely fill the cell was then added. The stainless steel rod was then inserted into the tapped hole, and the entire apparatus was suspended in the bath. For bath temperatures below ambient conditions, the cooling unit was turned on and the temperature then stabilized by adding the necessary amount of heat required to keep the temperature from dropping further. Bath temperatures above ambient conditions were all obtained by adjusting the heater with a thermoregulator. When a negligible ΔT across the annulus was noted, power was applied to the central heating element and the fluid ΔT was allowed to stabilize. The power supply, fluid ΔT, and temperature were then recorded.

The thermal conductivities of the borates were determined in the same manner as for benzene. However, because the borates hydrolyze upon contact with moist air, the cell was flooded with nitrogen before filling with the sample. The annulus was rinsed with methanol and then acetone and finally dried by means of a nitrogen purge after each borate.

Results and Discussion

The cell conduction heat losses are shown in Table I. The average loss for the 12 runs is 2 × 10^{-3} W/μV. This number has been used in all thermal conductivity calculations. A sample calculation is presented in the Appendix.

Figure 3 compares the measured thermal conductivities of benzene with the values reported by other investigators (*12*). The average error over the entire range of measured values has been calculated to be less than ±0.25%, indicating excellent agreement with the reported values.

Figure 4 shows the thermal conductivities of various borates as functions of temperature. A linear equation of the form

$$k = A + BT \tag{2}$$

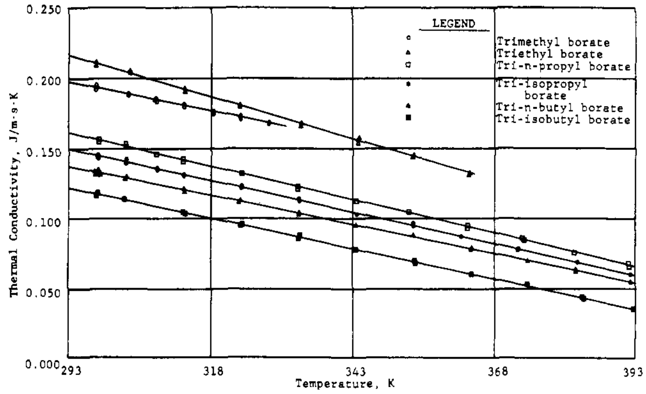


Figure 4. Thermal conductivity temperature dependence for trialkyl borates.

Table II. Constants for Equation 2 from Least-Squares Curve Fit

test liquid	$A \times 10$	$-B \times 10^4$	av % error
benzene	2.321	2.927	0.249
methyl borate	4.373	8.188	0.324
ethyl borate	5.567	11.630	0.535
n-propyl borate	4.450	9.649	0.434
isopropyl borate	4.144	9.009	0.852
n-butyl borate	3.802	8.281	0.925
isobutyl borate	3.794	8.759	0.551

was fitted to each set of data by a computer program. The coefficients A and B and the average relative percent error between the experimental and calculated values are given in Table II. In the absence of reported thermal conductivity values for the borates, the small errors between the measured values and those calculated by the curve fit may be taken as an indication of the reliability of the apparatus and the experimental procedure, at least for this class of compounds.

Figure 4 shows the thermal conductivities of the ethyl borate to be higher than those of the methyl borate. This is not particularly disturbing, as the first one or two members of many homologous series of compounds do not exhibit normal behavior (*7*). In a number of group contribution methods for estimating properties, the first few members of the homologous series have to be treated differently.

The calculation of thermal conductivity by the Fourier law assumes that all of the heat flows by conduction alone. The presence of natural convection and radiation will introduce an error in the computed values of thermal conductivity. The extent of natural convection present is indicated by the magnitude of the Rayleigh number. An upper limit of 1000–1200 for the Rayleigh number has been suggested in the literature (*1*, *6*) to ensure that the effects of natural convection will be small. The Rayleigh number, N_{Ra}, is the product of Prandtl number and Grashoff number and is given by

$$\begin{aligned} N_{\mathrm{Ra}} &= N_{\mathrm{Pr}} \cdot N_{\mathrm{Gr}} \\ &= \frac{C_p \beta \rho^2}{\mu k} \cdot g b^3 (\Delta T) \end{aligned} \tag{3}$$

where C_p is the specific heat, β the coefficient of volumetric expansion, ρ the density, μ the absolute viscosity, k the thermal conductivity, g the gravitational accleration, b the distance across the annulus, and ΔT the temperature drop across the annulus. The calculated Rayleigh numbers for methyl and ethyl borates, as well as those for all of the borates at high temperatures were greater than 1000. (This calculation requires estimation of C_p and β. The specific heats of most nonmetallic liquids lie in the range 0.84–4.19 J/(g K), with many being approximately 2.09 J/(g K) (*13*), whereas their coefficients of volume expansion are between 0.50 × 10^{-3} and 1.2 × 10^{-3} °C^{-1}, with many being approximately 1.00 × 10^{-3} °C^{-1} (*8*).) As a result, the thermal conductivities of the methyl and ethyl borates and those for all borates at higher temperatures will be subject to some error.

The presence of radiative heat transfer will also introduce an error into the measured values of thermal conductivities. The extent of radiative heat transfer present depends on the thickness of the liquid layer and on the optical qualities of the liquid and the surfaces surrounding it (*9*). A detailed analysis of the effects of radiation upon thermal conductivity in this apparatus was carried out by Baxley and Couper (*1*), who found that radiation heat transfer accounted for less than 0.5% of the total heat transfer. On the basis of the close agreement of the measured thermal conductivities of benzene with the values reported in the literature, it is believed that the radiative effects in this work have been small. It is further speculated that the combined effect of radiative and convective heat transfer may introduce an error of 10–15% in the measured thermal conductivities of the borates. Since the primary use of thermal conductivities is in engineering design, such error levels are quite acceptable.

Acknowledgment

The thermal conductivity cell was lent by Professor James R. Couper of the University of Arkansas. The authors thank Professor Robert N. Maddox of Oklahoma State University for his review and comments.

Appendix

The equation for the fluid thermal conductivity, k, is based on the Fourier law at steady state

$$k = q(\Delta r)/A(\Delta T) \tag{4}$$

where A = geometric average of the areas = $4\pi r_{1o} r_{2i}$, r_{1o} = outer radius of the inner = 0.0254 m, r_{2i} = inside radius of the outer sphere, 0.0298 m, Δr = thickness of the annular space, 0.004 445 m. The term ΔT is the temperature drop across the sample. But recall that while one thermocouple is located on the outside surface of the inner sphere, the other is located on the outside surface of outer sphere. Therefore, the corrected temperature difference, ΔT_c, which must be used in eq 4, is obtained by subtracting the temperature drop across the outer cell wall, ΔT_{cw}, from the observed temperature difference, ΔT_o. Thus

$$\begin{aligned} \Delta T_c &= \Delta T_o - \Delta T_{cw} \\ &= \Delta T_o - qc(\Delta r_{cell})/k_{cell} A_2 \end{aligned} \tag{5}$$

where

$$q_c = q_o - q_{loss} \tag{6}$$

q_{loss} = conduction heat loss through pins and leads = 0.002 W/μV × ΔT_o μV and Δr_{cell} = thickness of the outer cell wall (0.006 35 m), A_2 = geometric average of the areas ($4\pi r_{2i} r_{2o}$), r_{2i} = inside radius of the outer sphere (0.0298 m), r_{2o} = outside radius of the outer sphere (0.0362 m), and k_{cell} = thermal conductivity of stainless steel (15.58 J/m s K). Thus, the equation for corrected ΔT in degrees Kelvin becomes

$$\Delta T_c = 0.023 \Delta T_o - 0.030 q_c \tag{7}$$

In eq 5, q_c must be in watts and the constant 0.0230 represents a conversion factor between microvolts and degrees K. Substituting eq 5 and 7 in eq 4 gives a final equation for fluid thermal conductivity. Thus

$$k = \Delta r(q_o - 0.002(\Delta T_o))/A(0.023(\Delta T_o) - 0.030 q_c) \tag{8}$$

$$k = 0.004445(q_o - 0.002(\Delta T_o))/0.009512[0.023 \Delta T_o - 0.030(q_o - 0.002(\Delta T_o))]$$

By use of a sample data point for benzene with ΔT = 18.5 μV, q_o = (2.77 V)(0.060 A), eq 8 gives

$$k = 0.4673\{(2.77)(0.06) - (0.002)(18.5)\}/[(0.023) \times (18.5) - (0.03)\{(2.77)(0.060) - (0.002)(18.5)\}] = 0.1436 \text{ mW/(cm K)} = 0.1436 \text{ J/(m s k)}$$

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