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# Thermal Conductivities of Ternary Liquid Mixtures

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**A new, transient, hot-wire thermal conductivity cell has been constructed, calibrated against pure liquid toluene, and used to measure mixture thermal conductivity values in six ternary systems at 298 K and ambient pressure. These data have been used to test the accuracy of commonly used models/correlations that are both predictive in nature and extendable to multicomponent systems. For these six systems, the order of model accuracy was power law, local composition, Li, and ideal equations.**

## Introduction

Thermal conductivity values are essential in process design, development, and optimization in chemical and energy related industries. Because of the wide diversity in chemical constituency and conditions useful in these industries, predictive techniques are obviously desired. Development of these techniques, however, must be based on experimental measurements made on systems and at conditions definitive to the building, refining, and testing of the models and their assumptions, or they will probably lack generality and accuracy.

There have been a number of correlations proposed for liquid mixture thermal conductivity (*1-6*). These generally require pure component values and at least one mixture value (to fix the ubiquitous adjustable parameter required to account for system-specific interactions). A few of these correlations can be made predictive in nature if the adjustable parameter is fixed at some average value (*1-4*). While the predictive capabilities of the resultant models have been tested against binary thermal conductivity data, a paucity of ternary data has precluded testing against multicomponent liquid mixture values. Furthermore, many of the empirical models are applicable only to binary systems—their closed binary form is unextendable to ternary mixtures. Of those models referenced above, only the Li (*3*) and power law (*1*) equations can be applied to ternary systems. The few measurements of ternary liquid mixture thermal conductivity reported in the literature (*7*, *8*) were only used to test a mass-fraction-average model. Rowley (*9*) has recently shown the possibility of predicting mixture thermal conductivities from thermodynamic mixture properties. His model, based on the local composition concept, was developed for any number of components but was tested only against binary thermal conductivity data. Moreover, the local composition model for multicomponent systems utilizes only binary molecular interactions. This assumption also remains untested due to the lack of ternary experimental data.

To provide ternary mixture data with which to test various thermal conductivity models and with which to evaluate the validity of the binary-interaction assumption utilized in development of the local composition model, we report here ternary liquid thermal conductivities for six systems measured in a new transient hot-wire apparatus patterned after that of Perkins (*10*, *11*).

It should also be mentioned that considerable progress has been made in the development of corresponding states techniques for prediction of thermal conductivity. These methods have a wide range of temperature/pressure applicability, but lack accuracy in predicting the composition dependence unless adjustable parameters are used in the mixing rules. The data reported here should also be useful in refining mixing rules for corresponding states techniques.

## Experimental Section

The transient hot-wire technique is considered by many (*10*) to be the most precise method for measurement of liquid mixture thermal conductivity. It has been employed since the late 1930's. Its history of use, analysis assumptions, experimental techniques, error analysis, assets, and limitations have been carefully studied and are readily available (*12-16*). We report here only the particulars of the cell design, the data acquisition/analysis equipment, and the experimental procedures unique to this work.

The thermal conductivity cell used in this work was a single-wire cell, machined from 316 stainless steel and sealed with Viton O-rings. The platinum measurement wire, 0.0005 in. in diameter, was obtained from American Fine Wire Co. with the specifications of 99.95% purity and 266.8 ± 5% Ω/ft. A special cell insert, machined from thin-walled (0.04 in.), 0.50 in. o.d., stainless steel tubing, was employed to secure and align the wire in its axial position. Figure 1 shows a detailed sketch of one of the two identical ends of the cell with insert and end cap in place. Most of the walls of the insert were machined away as the purpose of the insert is strictly for wire-mounting purposes. The ends of the measurement wires were soldered to short lengths of 0.039-in.-diameter platinum leads. These leads were electrically insulated from the end caps by thin Teflon sheaths (A) and held in place in the insert with set screws (B). To minimize end effects, the low-resistance platinum leads projected approximately 1 cm into the open body of the insert and the measurement wires used were always at least 20 cm long. As shown in Figure 1, the ends of the insert were machined in a saddle shape (D) (a view perpendicular to that of Figure 1 would show the ends beveled up) to allow complete displacement of all air from the cell as it is filled with the liquid mixture from the bottom. The wire was carefully pulled taut and secured to both ends of the cell insert before final assembly of the cell.

With the wire fastened to the insert, the insert assembly was placed into the stainless steel cell (H) and end caps (I) were bolted to the body of the cell. Flanges (G) on either end of the insert served as vertical spacers; the end caps maintained radial alignment. The fluid seals in the assembled cell were made with O-rings (J) imbedded in machined grooves. The final fluid seal at the platinum lead exit was made by compression of O-ring (E) by a fitting screwed into bore (F). The O-ring also insulated the platinum wire from the stainless steel end cap. Electrical isolation within the fitting was achieved with Teflon tape.

The outer cell was machined from a 1.0-in.-o.d. (0.12-in-thick wall) tube, 9.3 in. in length. Two $^1/_{16}$-in. 216 stainless steel tubing ports (K) were welded into the end caps of the cell through which solution could be injected or withdrawn. The ports at the top of the cell were connected via $^1/_{16}$-in. tubing to a waste receptacle; the bottom ports were connected to $^1/_{16}$-in. tubing, coiled to serve as a heat exchanger and connected to luer-loc syringe valves mounted to the top bulkhead of a constant temperature water bath. The entire assembled cell was suspended from this bulkhead by means of threaded stainless steel rods as shown in Figure 2.

The water bath was a 50-L thermally insulated, double-walled, Gott water cooler that was further insulated in a plywood box. The box was attached to a cable-and-winch system capable

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**Table I. Equipment Specifications**

| item | label in Figure 2 | manuf | specifications |
|---|---|---|---|
| power supply | O | Hewlett Packard, Model 6114A | range, 0.01–39.99 V; increment, 0.01 V;<br>accuracy, 1 mV + 0.025% resolution, 200 $\mu$V |
| data acquisition | N | Keithley-DAS | A–D converter<br>accuracy, 14 bit<br>resolution, 35 $\mu$s<br>analog input board<br>channels, 32<br>settling time, 4 $\mu$s<br>power controller<br>channels, 4 |
| standard resistor | U (part of S) | Leeds & Northrup, NBS Type #4025-B | resistance, 9.99997 Ω<br>accuracy, ±0.003% |
| const temp baths | R and T | Neslab Endocal, Model RTE 8DD | control, ±0.002 K<br>stability, ±0.002 K |
| computer | V | IBM-PC | clock, 250 ns |
| quartz thermometer | G and M | Hewlett Packard, Model 2804A | resolution, ±0.1 mK<br>accuracy, ±0.04 K<br>calibration, IPTS-68 |
| temp controller | L | Bailey Instr., Model 252 | accuracy, ±1 mK<br>long-term control, ±1 mK |
| calibration multimeter |  | Hewlett Packard, Model 3456A | digits, 6.5<br>resolution, 0.1 mΩ; 0.1 $\mu$V<br>accuracy, 0.003% |
| 1st stage amp | P | Nat. Semicond., LH0038 | gain, 100X fixed<br>nonlinearity, 0.01% |
| 2nd stage amp | Q | Nat. Semicond., LF356 | gain, 1–20×<br>nonlinerity, 0.01% |

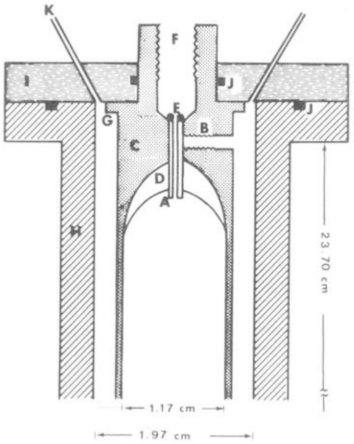

**Figure 1.** Schematic of cell end depicting (A) Teflon sheath; (B) extension wire set screw; (C) cell insert; (D) beveled end of insert; (E) wire-insert O-ring seal; (F) insert bore; (G) insert flange; (H) outer cell wall; (I) end cap; (J) O-ring seals.

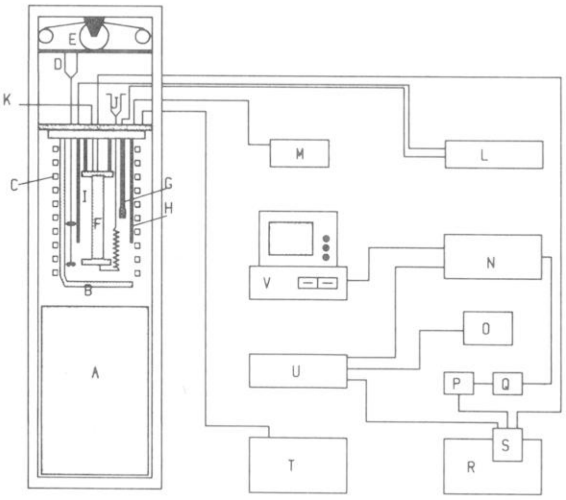

**Figure 2.** Schematic of apparatus including (A) water bath; (B) base heater; (C) cooling-water coils; (D) stirrer; (E) cable-pulley system; (F) cell; (G) thermometer probe; (H) control sensor; (I) control heater; (J) feed syringe; (K) overflow line; (L) temperature controller; (M) thermometer electronics; (N) data acquistion system; (O) power supply; (P) 1st-stage amplifier; (Q) 2nd-stage amplifier; (R) oil bath; (S) bridge circuitry; (T) water bath; (U) power controller; (V) IBM-PC computer.

of raising the bath up to the bulkhead for run position and lowering the bath to expose the cell for repairs. The constant temperature bath was controlled to ±0.002 K and served to provide uniform isothermal conditions in the fluid prior to application of the drive voltage. Listed in Table I are the manufacturers and their specifications for the temperature bath and peripheral electronic equipment shown diagramatically in Figure 2.

The Wheatstone bridge, of which the cell's measurement wire constitutes one of the four legs, was constructed with precision resistors of matched resistance, a Leeds-Northrup 4025-B, 9.99997 ± 0.00001 Ω standard resistor, and two precision 10-turn potentiometers with which to null the bridge. The entire bridge (S), excluding the cell, was immersed in an oil bath (R) maintained to ±0.001 K. All leads between the bridge and the cell and between the bridge and the data acquisition system were shielded, insulated, and, in the case of those in the water bath, enclosed in aluminum tubing.

Imbalance voltages from the experiments, on the order of 50 mV, were amplified with a two-stage amplifier. The first stage was a National Semiconductor LH0038 precision amplifier configured for a fixed gain of 100×; the second stage amplifier was a LF356 variable gain amplifier with a range of 1× to 20×. Bridge balancing prior to each run was performed with a coarse and a fine 10-turn potentiometer using a total gain of 2000×; measurements were made at 200×. The amplifier assembly was maintained in a shielded box and the amplifiers were zeroed at the beginning of each experiment. No long-term drift was detected in the amplifiers. Power was supplied to the amplifiers from the Keithley-DAS data acquisition system. The amplified imbalance voltage was converted from analog to digital by the 14-bit converter of the Keithley-Das system. With a maximum input voltage of ±10 V, the 14-bit accuracy of the converter allowed a maximum resolution of about 1.2 mV of the incoming signal. Experiments were performed at an optimum drive voltage to result in a temperature rise of 4.5–5.0 K.

Table II. Pure-Fluid Thermal Conductivities

| pure liq | $T$, K | exptl $k$, mW/(m·K) | $\sigma$ | lit. $k$, mW/(m·K) | investigator[a] |
|---|---|---|---|---|---|
| toluene | 293 | 133.81 | 0.33 | 134.8 | Brykov, 1970 |
| | | | | 133.0 | Pittman, 1968 |
| | | | | 134.4 | Ziebland, 1961 |
| | | | | 136.1 | Schmidt, 1954 |
| | | | | 134.9 | Reidel, 1951 |
| toluene | 303 | 129.74 | 1.26 | 128.1 | Mani, 1972 |
| | | | | 127.7 | Venart, 1971 |
| | | | | 131.9 | Brykov, 1970 |
| | | | | 128.8 | Tree, 1968 |
| | | | | 130.1 | Pittman, 1968 |
| | | | | 131.3 | Poltz, 1967 |
| | | | | 131.6 | Horrocks, 1963 |
| | | | | 131.6 | Ziebland, 1961 |
| | | | | 133.6 | Vargaftik, 1957 |
| toluene | 308 | 128.49 | 0.93 | 126.6 | Mani, 1972 |
| | | | | 126.3 | Venart, 1971 |
| | | | | 130.4 | Brykov, 1970 |
| | | | | 127.4 | Tree, 1968 |
| | | | | 128.7 | Pittman, 1968 |
| | | | | 131.3 | Poltz, 1967 |
| | | | | 130.2 | Horrocks, 1963 |
| | | | | 130.1 | Ziebland, 1961 |
| benzene | 298 | 142.70 | 0.38 | 142.4 | Poltz, 1967 |
| | | | | 142.1 | Poltz, 1965 |
| | | | | 142.1 | Horrocks, 1963 |
| | | | | 143.0 | Schmidt, 1954 |
| benzene | 308 | 135.69 | 0.97 | 139.2 | Poltz, 1967 |
| | | | | 138.8 | Horrocks, 1967 |
| | | | | 141.9 | Schmidt, 1954 |
| 1-butanol | 298 | 151.43 | 0.62 | 148.1 | Poltz, 1968 |
| | | | | 151.7 | Venart, 1967 |
| | | | | 152.42 | Riedel, 1951 |
| 2-butanone | 298 | 143.70 | 1.04 | 143.4 | Jobst, 1964 |
| $n$-butyl acetate | 298 | 136.20 | 0.52 | 136.9 | Mason, 1954 |
| carbon tetrachloride | 273 | 102.59 | 0.55 | 99.7 | Tree, 1968 |
| | | | | 107.0 | Challoner, 1954 |
| | | | | 102.6 | Mason, 1954 |
| | | | | 103.0 | Schmidt, 1954 |
| | | | | 103.5 | Riedel, 1951 |
| carbon tetrachloride | 298 | 100.59 | 0.28 | 98.7 | Tree, 1968 |
| | | | | 99.5 | Poltz, 1965 |
| | | | | 106.3 | Challoner, 1954 |
| | | | | 101.9 | Mason, 1954 |
| | | | | 102.5 | Schmidt, 1954 |
| | | | | 102.3 | Riedel, 1951 |
| carbon tetrachloride | 303 | 98.67 | 0.73 | 97.6 | Tree, 1968 |
| | | | | 105.7 | Challoner, 1954 |
| | | | | 101.2 | Mason, 1954 |
| | | | | 102.0 | Schmidt, 1954 |
| | | | | 101.1 | Riedel, 1951 |
| carbon tetrachloride | 308 | 97.66 | 0.35 | 96.5 | Tree, 1968 |
| | | | | 102.3 | Challoner, 1954 |
| | | | | 100.5 | Mason, 1954 |
| | | | | 101.5 | Schmidt, 1954 |
| | | | | 99.9 | Riedel, 1951 |
| chloroform | 298 | 113.29 | 0.36 | 115.15 | Mason, 1954 |
| cyclohexane | 298 | 120.53 | 0.52 | 120.95 | Taborek, 1971 |
| | | | | 119.21 | Horrocks, 1963 |
| | | | | 120.6 | Mukhamedzyanov, 1964 |
| $n$-heptane | 298 | 123.55 | 0.41 | 122.3 | Nagasaka, 1981[b] |
| | | | | 123.2 | de Castro, 1977[c] |
| | | | | 123.6 | Mukhamedzyanov, 1971 |
| | | | | 123.2 | Kerimov, 1970 |
| $n$-pentane | 298 | 112.45 | 0.53 | 112.4 | Mukhamedzyanov, 1971 |
| | | | | 112.6 | Brykov, 1970 |
| | | | | 110.5 | Bogatov, 1969 |
| 2-propanol | 298 | 135.66 | 0.60 | 134.45 | Jamieson, 1972 |
| | | | | 135.6 | Mallan, 1972 |
| | | | | 136.6 | Taborek, 1971 |
| | | | | 139.1 | Vasilkovskaya, 1969 |
| | | | | 134.4 | Poltz, 1967 |
| | | | | 140.0 | Riedel, 1951 |

[a] All but two investigators are cited in ref *5* of this paper. [b] Reference *18*. [c] Reference *19*.

This corresponds to an amplified bridge imbalance of over 9 V or an unamplified signal of 45 mV. Thus, the data acquisition system had a resolution of about ±6.0 $\mu$V in the actual signal corresponding to uncertainties in temperature-rise measurements on the order of about ±1.0 mK.

In accordance with the infinite line-source model in cylindrical coordinates, the temperature rise can be written as (*10*)

$$\Delta T = \frac{q}{4\pi k}\left[\ln\,(t) + \ln\left(\frac{4\alpha}{\gamma r^2}\right)\right] \qquad (1)$$

where $q$ is the heat input to the wire by the step-function drive voltage, $\Delta T$ is the temperature rise, $t$ is time in seconds, $k$ is thermal conductivity, $\alpha$ is thermal diffusivity, $\gamma$ = 1.7810, and $r$ is the wire radius. Typical raw output data from the experiments are displayed on a $\Delta T$ vs. ln ($t$) plot in Figure 3a. Temperatures were sampled at equal 2-ms intervals over a 800-ms interval. from eq 1, thermal conductivity can be obtained from linear least-squares analysis of the slope of $\Delta T$ vs. ln ($t$) and, in principle, thermal diffusivity can be obtained from the intercept. In practice it was found that small imbalance errors at the beginning of the experiment would affect the value of the intercept but not the slope. An error analysis of the apparatus and procedure indicates less than 1% uncertainty in the $k$ values but up to 20% in $\alpha$ values. Since there are better ways to measure $\alpha$ once $k$ is known, we report here only the measured thermal conductivities.

As mentioned, $\Delta T$ measurements were recorded over a 0.8-s time interval. Perkins (*10*) found that generally convection did not set in until later than 1.3 s and the correlation for the time of convection onset by Parsons and Mulligan (*14*) suggests that at least 1.5 s is required for our apparatus. Figure 3b shows that the onset of convection for our experiments begins at times much longer than the normal experimental runs. The characteristic lowering of the effective thermal conductivity (flattening of the slope in the figure) due to convection effects does not occur until nearly 4 s into the experiment. Thus, results reported here are deemed to be free of convection errors.

The temperature dependence of the thermal conductivity and radiation effects are most easily (*10*) corrected for by extrapolation of the slope of $\Delta T$ vs. ln ($t$) back to the start of the experiment. This was done by dividing the 400 data points for each run into 10 segments of 40 data points each. The slope of each segment was determined by using least-squares and then the slopes themselves were linearly fit vs. time. Correlation coefficients for the fit of each segment were within ±0.02 of 1.00 or else the segment was not included in the final extrapolation back to zero time. The first point was never included in the first segment as the finite heat capacity of the wire causes a noticeable error at short times; the first segment had a correlation coefficient of 1.000 or the run was discarded. A wire heat capacity correction by Healy et al. (*16*) was applied to the segments and found to be as large as 10% for times under 10 ms, but it rapidly drops to insignificant levels before

**Table III. Measured Values of Mixture Thermal Conductivities at 298 K and Ambient Pressure**

Toluene (1) + Carbon Tetrachloride (2) + Chloroform (3)

| $i$ | $j$ | $A_{ij}$ | $A_{ji}$ | $\alpha$ |
|---|---|---|---|---|
| 1 | 2 | −69.68 | 95.38 | 0.3041 |
| 1 | 3 | −583.62 | 629.22 | 0.2974 |
| 2 | 3 | 236.12 | 116.32 | 0.3029 |

| composition | | $k$, mW/(m·K) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $W_1$ | $W_2$ | exptl | ideal | % dev | Li | % dev | PL | % dev | LC | % dev |
| 1.00 | 0.00 | 132.03 | | | | | | | | |
| 0.00 | 1.00 | 100.59 | | | | | | | | |
| 0.00 | 0.00 | 111.47 | | | | | | | | |
| 0.60 | 0.20 | 116.16 | 121.63 | 4.7 | 124.37 | 7.1 | 119.28 | 2.7 | 119.19 | 2.6 |
| 0.20 | 0.60 | 102.98 | 109.06 | 5.9 | 111.49 | 8.3 | 107.29 | 4.2 | 106.72 | 3.6 |
| 0.20 | 0.20 | 108.20 | 113.41 | 4.8 | 115.36 | 6.6 | 112.14 | 3.6 | 111.84 | 3.4 |
| 0.40 | 0.40 | 108.99 | 115.34 | 5.8 | 118.55 | 8.8 | 111.19 | 2.0 | 112.35 | 3.1 |
| 0.40 | 0.20 | 111.77 | 117.52 | 5.1 | 120.29 | 7.6 | 113.80 | 1.8 | 115.30 | 3.2 |
| 0.20 | 0.40 | 105.73 | 111.23 | 5.2 | 113.43 | 7.3 | 109.63 | 3.7 | 109.16 | 3.2 |
| 0.33 | 0.33 | 107.76 | 114.70 | 6.4 | 117.55 | 9.1 | 112.57 | 4.5 | 112.16 | 4.1 |
| 0.50 | 0.50 | 111.14 | 116.31 | 4.7 | 119.94 | 7.9 | 113.16 | 1.8 | 112.65 | 1.4 |
| 0.50 | 0.00 | 117.56 | 121.75 | 3.6 | 124.06 | 5.5 | 120.45 | 2.5 | 120.53 | 2.5 |
| 0.00 | 0.50 | 104.55 | 106.03 | 1.4 | 106.06 | 1.4 | 105.61 | 1.0 | 105.37 | 0.7 |
| | | | | av 4.8 | | 7.0 | | 2.8 | | 2.8 |

Benzene (1) + $n$-Pentane (2) + Cyclohexane (3)

| $i$ | $j$ | $A_{ij}$ | $A_{ji}$ | $\alpha$ |
|---|---|---|---|---|
| 1 | 2 | 197.06 | 219.88 | 0.3008 |
| 1 | 3 | −2.28 | 302.81 | 0.3011 |
| 2 | 3 | −147.81 | 264.87 | 0.2994 |

| composition | | $k$, mW/(m·K) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $W_1$ | $W_2$ | exptl | ideal | % dev | Li | % dev | PL | % dev | LC | % dev |
| 1.00 | 0.00 | 142.06 | | | | | | | | |
| 0.00 | 1.00 | 112.45 | | | | | | | | |
| 0.00 | 0.00 | 120.01 | | | | | | | | |
| 0.60 | 0.20 | 125.33 | 131.73 | 5.1 | 129.31 | 3.2 | 129.71 | 3.5 | 131.86 | 5.2 |
| 0.20 | 0.60 | 117.51 | 119.88 | 2.0 | 118.00 | 0.4 | 118.47 | 0.8 | 120.23 | 2.3 |
| 0.20 | 0.20 | 118.01 | 122.91 | 4.2 | 121.60 | 3.0 | 121.82 | 3.2 | 122.95 | 4.2 |
| 0.40 | 0.40 | 121.39 | 125.81 | 3.6 | 123.13 | 1.4 | 123.71 | 1.9 | 126.14 | 3.9 |
| 0.40 | 0.20 | 120.83 | 127.32 | 5.4 | 125.30 | 3.7 | 125.59 | 3.9 | 127.35 | 5.4 |
| 0.20 | 0.40 | 112.42 | 121.40 | 8.0 | 119.70 | 6.5 | 120.11 | 6.8 | 121.64 | 8.2 |
| 0.33 | 0.33 | 118.22 | 124.84 | 5.6 | 122.63 | 3.7 | 123.04 | 4.1 | 125.05 | 5.8 |
| 0.50 | 0.50 | 122.00 | 127.26 | 4.3 | 123.88 | 1.5 | 124.69 | 2.2 | 127.81 | 4.8 |
| 0.50 | 0.00 | 125.20 | 131.04 | 4.7 | 129.87 | 3.7 | 129.65 | 3.6 | 130.65 | 4.4 |
| 0.00 | 0.75 | 113.09 | 114.34 | 1.1 | 114.00 | 0.8 | 114.21 | 1.0 | 114.54 | 1.3 |
| 0.00 | 0.50 | 114.68 | 116.23 | 1.4 | 115.76 | 0.9 | 116.05 | 1.2 | 116.51 | 1.6 |
| 0.00 | 0.25 | 117.08 | 118.12 | 0.9 | 117.74 | 0.6 | 117.98 | 0.8 | 118.34 | 1.1 |
| | | | | av 3.9 | | 2.5 | | 2.8 | | 4.0 |

Benzene (1) + Chloroform (2) + 2-Propanol (3)

| $i$ | $j$ | $A_{ij}$ | $A_{ji}$ | $\alpha$ |
|---|---|---|---|---|
| 1 | 2 | −418.99 | 376.71 | 0.2941 |
| 1 | 3 | 728.64 | 366.66 | 0.2910 |
| 2 | 3 | 1747.01 | −546.72 | 0.2962 |

| composition | | $k$, mW/(m·K) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $W_1$ | $W_2$ | exptl | ideal | % dev | Li | % dev | PL | % dev | LC | % dev |
| 1.00 | 0.00 | 142.06 | | | | | | | | |
| 0.00 | 1.00 | 112.62 | | | | | | | | |
| 0.00 | 0.00 | 137.57 | | | | | | | | |
| 0.60 | 0.20 | 134.16 | 135.27 | 0.8 | 136.92 | 2.1 | 133.55 | −0.5 | 133.70 | −0.3 |
| 0.20 | 0.60 | 118.34 | 123.50 | 4.4 | 126.61 | 7.0 | 121.46 | 2.6 | 120.76 | 2.0 |
| 0.20 | 0.20 | 131.22 | 133.48 | 1.7 | 135.20 | 3.0 | 132.01 | 0.6 | 132.13 | 0.7 |
| 0.40 | 0.40 | 125.89 | 129.39 | 2.8 | 132.16 | 5.0 | 127.08 | 0.9 | 126.82 | 0.7 |
| 0.40 | 0.20 | 131.98 | 134.38 | 1.8 | 136.04 | 3.1 | 132.77 | 0.6 | 132.93 | 0.7 |
| 0.20 | 0.40 | 124.13 | 128.49 | 3.5 | 131.35 | 5.8 | 126.41 | 1.8 | 126.10 | 1.6 |
| 0.33 | 0.33 | 126.64 | 130.75 | 3.3 | 133.26 | 5.7 | 128.74 | 1.7 | 128.53 | 1.5 |
| 0.50 | 0.50 | 121.52 | 127.34 | 4.8 | 130.29 | 7.2 | 124.81 | 2.7 | 124.52 | 2.5 |
| 0.50 | 0.00 | 139.10 | 139.81 | 0.5 | 139.66 | 0.4 | 139.76 | 0.5 | 140.06 | 0.7 |
| 0.00 | 0.75 | 115.43 | 118.86 | 3.1 | 121.69 | 5.4 | 117.57 | 1.9 | 116.61 | 1.1 |
| 0.00 | 0.50 | 128.97 | 125.09 | 3.4 | 128.39 | −0.5 | 123.24 | 1.9 | 122.67 | 1.4 |
| 0.00 | 0.25 | 128.97 | 131.33 | 1.8 | 133.52 | 3.5 | 129.82 | 0.7 | 129.80 | 0.6 |
| | | | | av 2.3 | | 4.0 | | 1.4 | | 1.2 |

**Table III** (Continued)

Toluene (1) + Benzene (2) + *n*-Pentane (3)

| $i$ | $j$ | $A_{ij}$ | $A_{ji}$ | $\alpha$ |
|---|---|---|---|---|
| 1 | 2 | -121.24 | 111.12 | 0.3033 |
| 1 | 3 | -490.42 | 1401.71 | 0.2980 |
| 2 | 3 | 197.06 | 219.88 | 0.3008 |

| composition | | $k$, mW/(m·K) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $W_1$ | $W_2$ | exptl | ideal | % dev | Li | % dev | PL | % dev | LC | % dev |
| 1.00 | 0.00 | 132.03 | | | | | | | | |
| 0.00 | 1.00 | 142.07 | | | | | | | | |
| 0.00 | 0.00 | 112.45 | | | | | | | | |
| 0.60 | 0.20 | 126.91 | 130.13 | 2.5 | 128.38 | 1.2 | 128.94 | 1.6 | 130.45 | 2.8 |
| 0.20 | 0.60 | 130.09 | 134.14 | 3.1 | 131.87 | 1.4 | 132.43 | 1.8 | 134.34 | 3.3 |
| 0.20 | 0.20 | 118.18 | 122.29 | 3.5 | 119.82 | 1.4 | 120.53 | 2.0 | 123.01 | 4.1 |
| 0.40 | 0.40 | 128.43 | 132.13 | 2.9 | 130.11 | 1.3 | 130.65 | 1.7 | 132.33 | 3.0 |
| 0.40 | 0.20 | 123.02 | 126.21 | 2.6 | 123.74 | 0.6 | 124.53 | 1.2 | 126.88 | 3.1 |
| 0.20 | 0.40 | 123.82 | 128.22 | 3.6 | 125.27 | 1.2 | 126.06 | 1.8 | 128.75 | 4.0 |
| 0.33 | 0.33 | 124.87 | 128.85 | 3.2 | 126.26 | 1.1 | 126.83 | 1.6 | 129.34 | 3.6 |
| 0.50 | 0.50 | 135.70 | 137.05 | 1.0 | 136.91 | 0.9 | 136.77 | 0.8 | 136.64 | 0.7 |
| 0.75 | 0.00 | 125.10 | 127.14 | 1.6 | 125.51 | 0.3 | 126.19 | 0.9 | 127.84 | 2.2 |
| 0.50 | 0.00 | 119.43 | 122.24 | 2.4 | 120.28 | 0.7 | 121.07 | 1.4 | 123.28 | 3.2 |
| 0.25 | 0.00 | 115.85 | 117.35 | 1.3 | 116.00 | 0.1 | 116.52 | 0.6 | 118.23 | 2.0 |
| 0.00 | 0.75 | 128.76 | 134.67 | 4.6 | 131.83 | 2.4 | 132.54 | 2.9 | 135.08 | 4.9 |
| 0.00 | 0.50 | 122.00 | 127.26 | 4.3 | 123.89 | 1.6 | 124.69 | 2.2 | 127.82 | 4.8 |
| 0.00 | 0.25 | 115.69 | 119.86 | 3.6 | 117.57 | 1.6 | 188.10 | 2.1 | 120.27 | 4.0 |
| | | | | av 2.9 | | 1.1 | | 1.6 | | 3.3 |

Cyclohexane (1) + Carbon Tetrachloride (2) + 2-Propanol (3)

| $i$ | $j$ | $A_{ij}$ | $A_{ji}$ | $\alpha$ |
|---|---|---|---|---|
| 1 | 2 | 434.75 | -327.06 | 0.2871 |
| 1 | 3 | 1229.94 | 616.95 | 0.5341 |
| 2 | 3 | 1174.62 | 91.33 | 0.2873 |

| composition | | $k$, mW/(m·K) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $W_1$ | $W_2$ | exptl | ideal | % dev | Li | % dev | PL | % dev | LC | % dev |
| 1.00 | 0.00 | 120.09 | | | | | | | | |
| 0.00 | 1.00 | 100.74 | | | | | | | | |
| 0.00 | 0.00 | 138.74 | | | | | | | | |
| 0.60 | 0.20 | 115.72 | 119.95 | 3.7 | 121.61 | 5.1 | 118.10 | 2.1 | 116.82 | 1.0 |
| 0.20 | 0.60 | 105.28 | 112.21 | 6.6 | 116.13 | 10.3 | 109.51 | 4.0 | 107.58 | 2.2 |
| 0.20 | 0.20 | 122.46 | 127.41 | 4.0 | 129.69 | 5.9 | 124.28 | 1.5 | 123.98 | 1.2 |
| 0.40 | 0.40 | 110.15 | 116.08 | 5.4 | 119.20 | 8.2 | 113.56 | 3.1 | 111.68 | 1.4 |
| 0.40 | 0.20 | 118.49 | 123.68 | 4.4 | 125.58 | 6.0 | 121.07 | 2.2 | 120.13 | 1.4 |
| 0.20 | 0.40 | 113.79 | 119.81 | 5.3 | 123.59 | 8.6 | 116.20 | 2.1 | 114.84 | 0.9 |
| 0.33 | 0.33 | 113.99 | 119.86 | 5.2 | 122.87 | 7.8 | 116.99 | 2.6 | 115.31 | 1.2 |
| 0.50 | 0.50 | 105.33 | 110.42 | 4.8 | 113.34 | 7.6 | 109.15 | 3.6 | 107.73 | 2.3 |
| 0.50 | 0.00 | 125.27 | 129.42 | 3.3 | 129.04 | 3.0 | 128.41 | 2.5 | 128.56 | 2.6 |
| 0.00 | 0.50 | 114.77 | 119.74 | 4.3 | 124.80 | 8.7 | 115.28 | 0.4 | 114.51 | -0.2 |
| | | | | av 4.7 | | 7.1 | | 2.4 | | 1.4 |

*n*-Pentane (1) + Toluene (2) + 2-Propanol (3)

| $i$ | $j$ | $A_{ij}$ | $A_{ji}$ | $\alpha$ |
|---|---|---|---|---|
| 1 | 2 | 1401.71 | -490.42 | 0.2980 |
| 1 | 3 | -122260.74 | 1029.67 | 0.7652 |
| 2 | 3 | 1316.32 | 693.78 | 0.5912 |

| composition | | $k$, mW/(m·K) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $W_1$ | $W_2$ | exptl | ideal | % dev | Li | % dev | PL | % dev | LC | % dev |
| 1.00 | 0.00 | 112.91 | | | | | | | | |
| 0.00 | 1.00 | 132.03 | | | | | | | | |
| 0.00 | 0.00 | 139.81 | | | | | | | | |
| 0.60 | 0.20 | 119.77 | 122.12 | 2.0 | 120.05 | 0.2 | 120.59 | 0.7 | 122.41 | 2.2 |
| 0.20 | 0.60 | 128.22 | 129.77 | 1.2 | 128.20 | 0.0 | 128.74 | 0.4 | 129.96 | 1.4 |
| 0.20 | 0.20 | 131.32 | 132.88 | 1.2 | 130.82 | -0.4 | 131.47 | 0.1 | 132.67 | 1.0 |
| 0.40 | 0.40 | 123.09 | 125.94 | 2.3 | 123.79 | 0.6 | 124.46 | 1.1 | 126.37 | 2.7 |
| 0.40 | 0.20 | 124.35 | 127.50 | 2.5 | 125.07 | 0.6 | 125.68 | 1.1 | 127.46 | 2.5 |
| 0.20 | 0.40 | 129.92 | 131.32 | 1.1 | 129.53 | -0.3 | 130.08 | 0.1 | 131.29 | 1.1 |
| 0.33 | 0.33 | 125.26 | 128.25 | 2.4 | 126.04 | 0.6 | 126.79 | 1.2 | 128.39 | 2.5 |
| 0.50 | 0.50 | 119.42 | 122.47 | 2.6 | 120.56 | 1.0 | 121.35 | 1.6 | 123.49 | 3.4 |
| 0.50 | 0.00 | 122.76 | 126.36 | 2.4 | 123.71 | 0.8 | 124.23 | 1.2 | 125.76 | 2.4 |
| 0.00 | 0.50 | 135.47 | 135.92 | 0.3 | 135.51 | 0.0 | 135.75 | 0.2 | 135.55 | 0.1 |
| | | | | av 1.8 | | 0.5 | | 0.8 | | 1.9 |

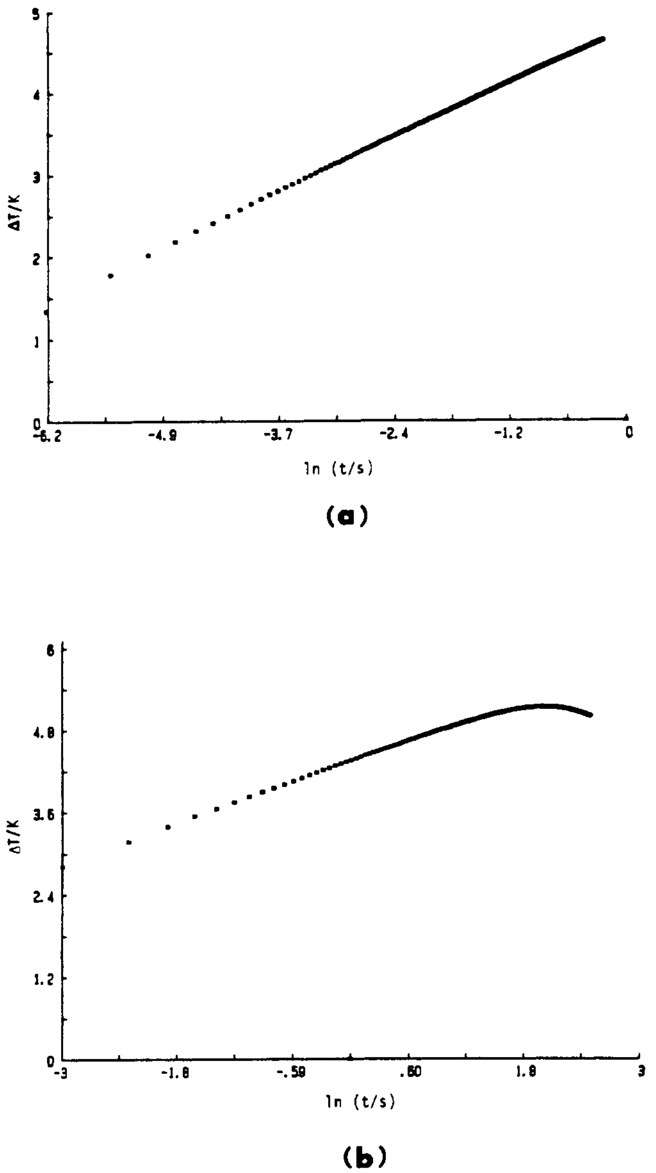

**Figure 3.** Typical experimental data of $\Delta T$ vs. ln ($t$) showing (a) the linear behavior for normal run times of 0.8 s, and (b) the onset of convection at much longer times.

40 ms. Other corrections were found to be insignificant because of cell design and the short measurement time. According to the requirements derived by Kierkus et al. (*17*), the infinite heat source assumption is satisfied for our apparatus for wires longer than 13.4 cm. As mentioned, all wires used in the cell were at least 20 cm in length and axial conduction can be neglected. Axial conduction errors were checked by using the method of Perkins (*10*) and found to be insignificant in all cases. The assumption of a constant heat production rate in the wire was also found to be valid. During the experiment, a 5 K temperature increase resulted in a 1.7% increase in the resistance of the wire and a 0.9% drop in the applied voltage across the wire resulting in a 0.1% change in the heat rate of the wire. As the average power for each segment was used in the data analysis the overall effect on the thermal conductivity was found to be less than 0.0025%. Solution of the thermal conduction problem for the wire indicated that the isothermal wire assumption was also valid to about the resolution of our temperature measurements (3 mK maximum radial temperature difference). McLaughlin and Pittman (*15*) and Healy et al. (*16*) have derived geometrical conditions for neglect of bounded-medium errors. Over the 0.8-s experimental run time, their criteria are satisfied by several orders of magnitude and thermal penetration is much less than the cell radial size.

Mixtures were prepared volumetrically, mixed in closed flasks at room temperature, and immediately infused into the bottom of the cell until fluid appeared in the waste lines. Measurements were repeated between five and ten times from which a standard deviation was determined. Additionally, some points were checked by refilling the cell with a newly prepared mixture and repeating the thermal conductivity measurements.

### Equipment Calibration

The resistance of the cell measurement wire was measured as a function of temperature from 288 to 318 K in 2.5 K increments. The measurements were made using the four-lead method and an HP 3456A multimeter. A quadratic function was fitted with least squares to the measured resistances, and agreement between the correlation and measured resistances was better than 0.01% at each temperature.

Although the wire length was measured with calipers after installation into the insert and then remeasured once the cell was assembled, using the above-mentioned temperature–resistance correlation, the two wire lengths did not agree within the desired accuracy of less than 1%. Instead, the wire length was calibrated by performing thermal conductivity measurements on pure toluene and backing out the wire length from the well-known value. This procedure also eliminates any spurious junction and lead resistance problems. Fischer Scientific A.C.S. spectrophotometric grade toluene (purity > 99.99%) was used as a calibration standard. Twenty measurements of toluene's thermal conductivity at 298 K were made and compared to a value of 132.035 mW/(m °C) obtained by averaging literature values deemed by Jamieson (*5*) to be of the highest quality. It was found that the wire length differed from the previous equilibrium resistance measurement by about 8%. That is, a calibration coefficient of 0.921 878 7 was used in conjunction with the previously determined wire length.

To confirm that the calibration constant was valid for other temperatures, fluids, and power inputs, the thermal conductivities of pure components were measured and compared to those data compiled by Jamieson and deemed most reliable. Table II shows a comparison of pure component thermal conductivities. Values measured with this instrument are, in general, bracketed by the measurements of previous studies. Overall, measured values agree with those most recently reported in the literature to about ±2%, about the same as the experimental uncertainty indicated by Jamieson. Measurements were also made over a limited temperature range on some of the more extensively studied fluids to ensure temperature independence of the calibration constant. These values are also reported in Table II and compared to earlier studies. It is evident from these results that the cell calibration constant is independent of temperature and constituency and is indeed an apparatus constant. A complete error analysis has been reported elsewhere for this apparatus (*20*). We believe all values to be accurate to 1%.

### Results and Discussion

Six ternary systems were studied in this work at 298.15 K and ambient pressure. Thermal conductivities were measured for each of the three pure components and for at least one of each of the constituent binary pairs. Additionally, seven ternary compositions were measured. The results are compiled in Table III, and predictions by various models extendable to ternary mixtures are compared to them. The ideal method is a mass fraction average of the pure component values

$$k = \sum_{i=1}^{3} w_i k_i \qquad (2)$$

where $w_i$ is mass fraction of component $i$ and $k_i$ is pure component thermal conductivity of component $i$. The Li (*3*) equation is based on volume fraction, $\phi$, and values shown in Table III were computed by using pure component density values tabulated in ref *1* in conjunction with

$$k = \sum_{i=1}^{3}\sum_{j=1}^{3}\phi_i\phi_j k_{ij}; \quad k_{ij} = 2(k_i^{-1} - k_j^{-1})^{-1} \tag{3}$$

The power law (PL) equation, a modification of the ideal equation, is

$$k^{-2} = \sum_{i=1}^{3} w_i k_i^{-2} \tag{4}$$

The local composition (LC) model (*9*) treats deviations from eq 2 in terms of deviations of the local composition from random mixing, these being determined from equilibrium properties. The local compositions are found from

$$k = \sum_{i=1}^{3} w_i \sum_{j=1}^{3} k_{ji} w_j G_{ji} / (\sum_{m=1}^{3} w_m G_{mi}) \tag{5}$$

where the $k_{ji}$ and $G_{ji}$ can be calculated from the following relations:

$$k_{ji} = (w_i{}^* w_{ii}{}^* k_i + w_j{}^* w_{jj}{}^* k_j)/(w_i{}^* w_{ii}{}^* + w_j{}^* w_{jj}{}^*) \tag{6}$$

$$w_i{}^* = (M_i G_{ji}{}^{.5})/(M_i G_{ji}{}^{.5} + M_j G_{ji}{}^{.5}); \quad w_{ii}{}^* = w_i{}^*/(\sum_{m=1}^{3} w_i{}^* G_{mi}) \tag{7}$$

$$G_{ji} = \exp(-\alpha A_{ji}/RT); \quad G_{ii} = 1 \tag{8}$$

The interaction terms, $A_{ji}$ and $\alpha$, used to obtain the values reported in Table III, are included in the table and were obtained from a compilation of NRTL parameters for vapor–liquid equilibrium data (*21*).

The results of Table III are as yet inconclusive and more ternary experiments are currently being performed by using this new apparatus. Overall average absolute deviations for the ideal, Li, LC, and PL models are 3.4%, 3.7%, 2.4%, and 2.0%, respectively. The LC model does predict accurately for four of the six systems but performs badly on the other two. Whether these results really reflect the neglect of ternary interactions in the model or are an artifact of either the relatively small number of systems compared in this study or erroneous NRTL constants is yet unclear and needs further investigation. Rather surprisingly, these initial tests of multicomponent thermal conductivity indicate that the PL model predicts mixture values relatively well considering its simplicity and lack of any interaction information whatsoever.

## Conclusions

We have measured thermal conductivities of six ternary liquid mixtures in a new, transient, hot-wire thermal conductivity cell. The cell has been calibrated and tested against well-known values for pure fluids and the uncertainty in measured thermal conductivity values is expected to be ±1% to ±2% based on the comparison of pure fluid values shown in Table II and the reproducibility of the measurements. The cell design and operation conform to the criteria established by others for conformity to the assumptions of the infinite, line-heat-source model. The results of this study have been used to test predictions of the relatively few predictive models which are extendable to ternary mixtures. It was found that the ideal model yields unsatisfactory predictions and that the Li and LC models can fail significantly on some mixtures. The PL model gave the most consistent results for these six systems. However, the PL model is reported to be accurate only when the ratios of pure component thermal conductivities are between one and two, which is the case with all of the systems tested herein. Further ternary studies are required to distinguish between the accuracies of these two models and further test the neglect of ternary interactions in the local composition model.

**Registry No.** Toluene, 108-88-3; carbon tetrachloride, 56-23-5; chloroform, 67-66-3; benzene, 71-43-2; *n*-pentane, 109-66-0; cyclohexane, 110-82-7; 2-propanol, 67-63-0.

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