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Thermal Conductivity of Liquid Propane

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The paper presents new experimental measurements of the thermal conductivity of liquid propane for seven isotherms from 110 to 300 K with pressures to 70 MPa, i.e., a total density range of 11-16.5 mol/L (484-726 kg/m^3). It is estimated that the overall uncertainty in the thermal conductivity is 1.5%. The data can be represented with an equation which is based on an existing correlation. The data are compared to the experimental measurements of others in the liquid state. Values for the saturated liquid are established by using the equation.

Introduction

Measurements of the thermal conductivity of liquid propane are few (*1-4*), and those that do exist do not cover a very extensive range of densities for a given isotherm. A recent review and correlation (*5*) points out that it would be helpful if the more modern experimental techniques to measure transport properties could be applied to propane, and it is stressed that the data base for propane in particular should be improved. Since it appears that the behavior of propane is typical of the higher aliphatic hydrocarbons, new results might be especially useful. In this paper new experimental measurements are presented which, in contrast to earlier work, cover a large range in density for every isotherm, i.e., pressures from near 0 to 70 MPa (0-10000 psi). The new results are used with the existing correlation to improve the accuracy of that correlation especially at low temperatures and high densities.

Experimental Section

The measurements were made with a new transient hot-wire thermal-conductivity apparatus which is described elsewhere (*6*, *7*). In the transient hot-wire technique (*8-11*), a thin platinum wire immersed in the fluid and initially in thermal equilibrium with it is subjected at time $t = 0$ to a step voltage. The wire will behave as a line source of heat with constant heat generation. The physical arrangement closely models an ideal line source, and the working equation for the temperature increase in the wire, ΔT, is given by

$$\Delta T = \frac{q}{4\pi\lambda} \ln \left(\frac{4K}{a^2 C} t \right) \qquad (1)$$

where q is the heat generated per unit length of wire of radius a, $K = \lambda/(\rho C_p)$ is the thermal diffusivity of the fluid at the bath temperature, and $\ln C = \gamma$, where γ is Euler's constant. Corrections to eq 1 have been fully described elsewhere (*12*), the most important one being the effect of the finite heat capacity of the wire. All rare gases and many simple fluids are optically transparent. Most other fluids absorb, and for these fluids a second correction, which accounts for heat transfer by radiation, becomes important. An exact solution of the radiation correction for the hot-wire method is not yet at hand. However, numerical estimates for liquids that absorb such as *n*-heptane (*13*) and *n*-octane and *n*-decane (*14*) show that the effect is small, ca. 0.4% by one method (*15*, *14*) and 1.5% by the second one (*13*). For propane a lack of the pertinent optical data means that the present thermal-conductivity values are not corrected for the effect of radiation.

Use of a Wheatstone bridge provides end-effect compensation, while the voltages are measured directly with a fast-response digital voltmeter (DVM). The DVM is controlled by a minicomputer which also handles the switching of the power and the logging of the data. The measurement of thermal conductivity for a single point is accomplished by balancing the bridge as close to null as is practical at the cell or bath temperature. The lead resistances, the hot-wire resistances, and the ballast resistors are read first; then the power supply is set to the desired power, and the voltage developed across the bridge as a function of time is read and stored. The basic data form a set of 250 voltage readings taken at 3-ms intervals. The other variables measured include the applied power, the cell temperature, and the pressure. All of the pertinent data are written by the minicomputer onto a magnetic tape for subsequent evaluation.

For each run the data on the magnetic tape are processed on a large computer. In addition to the reduction of the raw data, i.e., the conversion of bridge offset voltages to resistance changes and then to temperature changes, the large computer also handles the wire calibration data and evaluates the best straight line for the ΔT-ln t data and determines the thermal conductivity. For the wire calibration some 1800 values were collected for each wire in the temperature range 77-320 K during an extended set of measurements on liquid oxygen (*16*).

The sample used was research-grade propane stated by the supplier to be 99.98 mol % propane with a trace of ethane. We used a small diaphragm compressor as a pressure intensifier. Normal safety precautions for high pressure and high vacuum were observed.

Results

In all, some 400 points were measured. A representative set of these measurements is shown in Table I. The entire set of measurements has been deposited as supplementary material. (See paragraph at end of text regarding supplementary material.) The measurements are distributed among seven pseudoisotherms where the nominal isotherm temperatures are 111, 139, 169, 196, 227, 260, and 299 K. There are roughly 60 points per isotherm taken at 10 different pressure levels, with several different power levels at each pressure. The temperature of measurement varies with the applied power so that the "isotherms" are nominal isotherms only. In Table I the reported pressure, temperature, and applied power are measured directly, the thermal conductivity and the associated regression error are obtained through the data reduction program, while the density is calculated from an equation of state for propane (*17*) by using the measured pressure and temperature. The last column in Table I shows the deviation of

Table I. Representative Set of Actual Experimental Thermal-Conductivity (TC) Values for Propane

press., MPa	temp, K	density, mol/L	power, W/m	TC, W/(m K)	STAT	exptl − calcd, %
67.411	226.290	14.45	0.590 31	0.1696	0.011	−0.76
67.413	227.015	14.44	0.802 40	0.1698	0.007	−0.44
67.414	227.870	14.42	1.047 21	0.1687	0.005	−0.80
67.414	228.719	14.41	1.325 06	0.1690	0.003	−0.40
67.411	225.440	14.46	0.333 44	0.1697	0.028	−0.93
67.411	225.956	14.45	0.496 50	0.1695	0.015	−0.87
67.41[a]	227.261[b]	14.432[c]		0.1692[d]	0.17[e]	−0.69[f]

[a] Average pressure. [b] Average temperature. [c] Average density. [d] Adjusted thermal conductivity. [e] Nominal reproducibility (rms %). [f] Deviation of adjusted thermal-conductivity value from correlation (%).

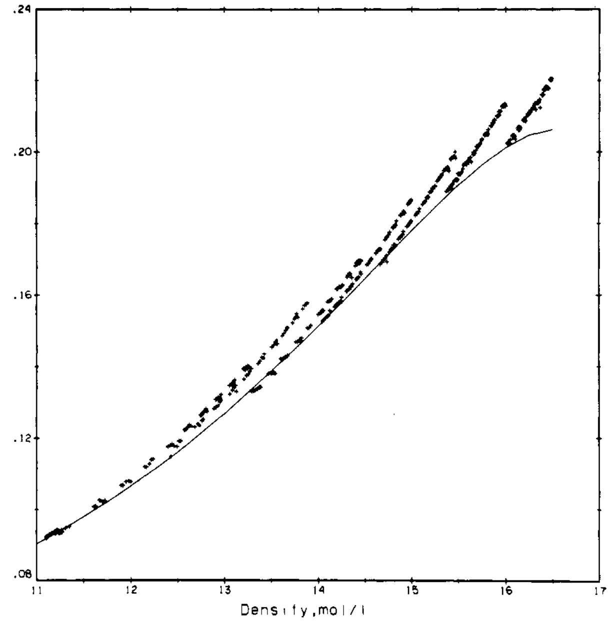

Figure 1. Thermal conductivity of propane vs. density.

each individual point from the correlating equation (next section) which represents the thermal-conductivity surface. The entire set of data is shown in thermal conductivity vs. density coordinates in Figure 1. Shown as a line in Figure 1 is the extrapolation of the thermal-conductivity surface to saturated-liquid conditions. It should be noted that any thermal-conductivity measurement imposes a temperature gradient. This implies that measurements can not be taken at saturation conditions, but rather, to avoid boiling, measurements must be made in the single-phase compressed fluid. If the thermal conductivity of saturated liquid is desired, an extrapolation has to be invoked.

To conserve space, Table II gives a summary of values where the multiple thermal-conductivity measurements for a given pressure level were first adjusted to an average temperature and an average density and then averaged. The last line in Table I along with the footnote indicates how the representative set of data in Table I was reduced to a single line for Table II. The variation in applied power can no longer be shown. The column STAT becomes a nominal reproducibility which is calculated as the rms percentage from the adjusted thermal-conductivity values.

Correlation of the Data

It is generally accepted that the thermal conductivity should be correlated in terms of density and temperature rather than temperature and pressure because, over a wide range of experimental conditions, the behavior of thermal conductivity is dominated by its density dependence. This preferred technique requires an equation of state (*17*) to translate measured pressures into equivalent densities. The dependence of thermal conductivity on temperature and density is expressed in ref *5* as

$$\lambda(\rho,T) = \lambda_0(T) + \lambda_1(T)\rho + \Delta\lambda(\rho,T) + \Delta\lambda_c(\rho,T) \quad (2)$$

where

$$\lambda_0 = g_1T^{-1} + g_2T^{-2/3} + g_3T^{-1/3} + g_4 + g_5T^{1/3} + g_6T^{2/3} + g_7T + g_8T^{4/3} + g_9T^{5/3} \quad (3)$$

$$\lambda_1(T) = A + B[C - \ln(T/F)]^2 \quad (4)$$

$$\Delta\lambda(\rho,T) = D\exp[k_1 + k_2/T]\{\exp[\rho^{0.1}(k_3 + k_4/T^{3/2}) + \theta\rho^{0.5}(k_5 + k_6/T + k_7/T^2)] - 1.0\} \quad (5)$$

with $\theta = (\rho - \rho_c)/\rho_c$. We retain eq 3 and 4 exactly as given in ref *5*. For the excess function, eq 5, we retain the functional form developed in ref *5* but vary the coefficients to give a best fit to all 400 points of the new liquid data. We neglect the critical contribution, $\Delta\lambda_c(\rho,T)$, because the new data are not close enough to the critical point to display a critical enhancement. Old coefficients for eq 3 and 4 and new coefficients for eq 5 are given in Table III.

Discussion

The precision of the apparatus can be established from several considerations. These are the linear regression statistics for a single point (the column STAT in Table I), the variation in the measured thermal conductivity with applied power, and the variation obtained in a curve fit of the thermal-conductivity surface considering different densities and different temperatures. All of these lead to a value of precision or reproducibility of a single measurement between ±0.6% and ±1.0%. The accuracy of the measurement can in principle be established from the measurements and certain theoretical considerations, i.e., for the rare gases the Eucken factor (*7*). Accuracy can also be estimated by comparison to the results of others. For the present apparatus these intercomparisons are 1% for helium (*6*), 1% for oxygen (*16*), and 1% for argon (*7*).

For propane the accuracy of the measurements in the liquid phase is limited by the simultaneous heat transfer by radiation, not accounted for in the experimental data. We estimate, in the absence of the exact calculations, a 0.5% error in the thermal conductivity caused by radiation. We compare the revised correlation to (a) the data presented in this paper and (b) the results of others. Shown in the upper part of Figure 2 are the deviations between the present measurements and the calculated thermal-conductivity surface, a plot of the last column of the full Table I vs. density. All of the deviations fit within a band of ±2%, shown as the dashed lines in the lower part of Figure 2, while the overall deviation is ±1.2% at the 2σ (95%) confidence level. The comparision to the results of others is shown in the lower part of figure 2 and is summarized in Table IV. The data used from ref 1 can be compared only

Table II. Summary of Thermal-Conductivity Values for Propane

av press., MPa	av temp, K	av density, mol/L	adj TC,[a] W/(m K)	nominal reproducibility, rms %	deviation of adj TC[a] value from corr, %
67.41	227.261	14.432	0.1692	0.17	−0.69
59.54	227.191	14.336	0.1655	0.42	−0.82
52.28	227.488	14.235	0.1622	0.18	−0.66
44.80	227.566	14.128	0.1583	0.15	−0.79
38.30	227.284	14.032	0.1551	0.11	−0.75
30.89	227.646	13.907	0.1509	0.20	−0.85
23.81	226.964	13.794	0.1472	0.17	−0.92
16.03	227.028	13.642	0.1424	0.30	−1.00
9.61	226.734	13.512	0.1381	0.43	−1.33
2.89	227.152	13.345	0.1335	0.27	−1.18
67.51	298.362	13.233	0.1395	0.22	−0.44
59.64	298.637	13.086	0.1355	0.17	−0.34
52.26	298.935	12.936	0.1312	0.20	−0.47
44.95	298.883	12.778	0.1271	0.32	−0.34
37.61	298.632	12.608	0.1229	0.16	−0.19
30.49	298.449	12.417	0.1179	0.16	−0.44
23.17	298.503	12.196	0.1130	0.42	−0.29
16.45	298.731	11.948	0.1074	0.35	−0.43
9.64	298.274	11.666	0.1017	0.41	−0.31
3.22	299.463	11.270	0.0941	0.18	−0.59
67.12	169.581	15.446	0.1987	0.32	0.05
59.26	169.612	15.375	0.1953	0.32	−0.20
51.75	169.612	15.303	0.1929	0.12	0.07
44.34	169.639	15.230	0.1898	0.10	−0.03
37.07	169.638	15.152	0.1867	0.18	−0.02
29.26	169.811	15.064	0.1831	0.14	−0.21
21.89	169.678	14.978	0.1800	0.08	−0.12
14.94	169.724	14.888	0.1767	0.19	−0.11
7.78	169.501	14.798	0.1734	0.16	−0.11
1.04	169.392	14.708	0.1698	0.40	−0.34
66.74	139.669	15.983	0.2131	0.14	0.56
59.97	139.716	15.933	0.2108	0.22	0.48
51.49	139.676	15.872	0.2082	0.21	0.45
43.27	139.714	15.803	0.2052	0.20	0.38
35.91	139.980	15.732	0.2027	0.28	0.52
29.32	139.774	15.680	0.2005	0.28	0.52
22.79	139.796	15.617	0.1976	0.33	0.34
15.26	139.868	15.543	0.1952	0.39	0.56
8.48	139.818	15.473	0.1923	0.27	0.46
2.60	139.897	15.407	0.1899	0.16	0.49
65.51	112.175	16.486	0.2204	0.08	−0.21
58.22	112.296	16.439	0.2180	0.11	−0.40
51.09	111.902	16.402	0.2166	0.27	−0.23
43.81	111.912	16.354	0.2139	0.43	−0.56
37.23	111.939	16.308	0.2127	0.29	−0.23
29.94	112.051	16.255	0.2109	0.20	−0.07
23.09	111.902	16.208	0.2091	0.21	0.01
15.51	111.919	16.148	0.2066	0.21	−0.02
8.39	112.039	16.088	0.2044	0.29	0.02
2.40	112.005	16.038	0.2027	0.17	0.14
67.90	196.020	14.982	0.1860	0.10	0.12
61.06	196.445	14.902	0.1828	0.08	0.01
53.56	196.462	14.820	0.1796	0.22	0.00
46.48	196.180	14.746	0.1765	0.15	−0.11
38.80	196.252	14.648	0.1726	0.10	−0.27
30.81	195.959	14.550	0.1694	0.15	−0.05
22.92	196.011	14.436	0.1653	0.27	−0.09
16.40	196.012	14.338	0.1619	0.16	−0.06
9.05	196.055	14.217	0.1577	0.27	−0.15
1.95	196.085	14.087	0.1538	0.28	0.04
68.06	260.986	13.865	0.1571	0.18	1.15
60.41	260.584	13.760	0.1535	0.42	1.07
53.46	260.558	13.652	0.1498	0.31	0.97
46.46	260.201	13.538	0.1463	0.36	1.07
39.29	260.678	13.398	0.1420	0.31	1.06
32.18	260.776	13.252	0.1379	0.32	1.19
24.92	260.433	13.098	0.1335	0.59	1.18
18.29	260.532	12.932	0.1292	0.24	1.41
11.37	260.626	12.738	0.1241	0.33	1.35
3.86	260.786	12.486	0.1177	0.90	1.23

[a] Adjusted thermal conductivity.

Table III. Coefficients for Eq 3-5[a]

eq 3	eq 4	eq 5
$g_1 = -0.1089381103E+07$	$A = -1.149813131$	$D = 1.0$
$g_2 = 0.8343297829E+06$	$B = 0.788531221$	$g_1 = -0.578825E+1$
$g_3 = -0.2270902736E+06$	$C = 1.12$	$g_2 = 0.181340E+3$
$g_4 = 0.1667866368E+05$	$F = 358.9$	$g_3 = 0.963981E+1$
$g_5 = 0.4347320565E+04$		$g_4 = -0.130794E+4$
$g_6 = -0.1177734671E+04$		$g_5 = 0.114745E+1$
$g_7 = 0.1215425833E+03$		$g_6 = -0.982209E+2$
$g_8 = -0.6040596921E+01$		$g_7 = 0.476504E+4$
$g_9 = 0.1207373681E+00$		$\rho_c = 0.221$ g/cm^3 (5.011 mol/L)

[a] Units: temperature in K, density in g/cm^3, thermal conductivity in mW/(m K).

Table IV. Deviations between Experimental Thermal Conductivities and the Calculated Surface from Ref 1-5

ref	no. of points	differences, % lowest	differences, % highest
1	14	−5.6	+4.7
2	49	−5.3	+1.7
3	10	−5.3	−2.6
4	14	−0.3	+1.6
5	20	−2.4	+5.6

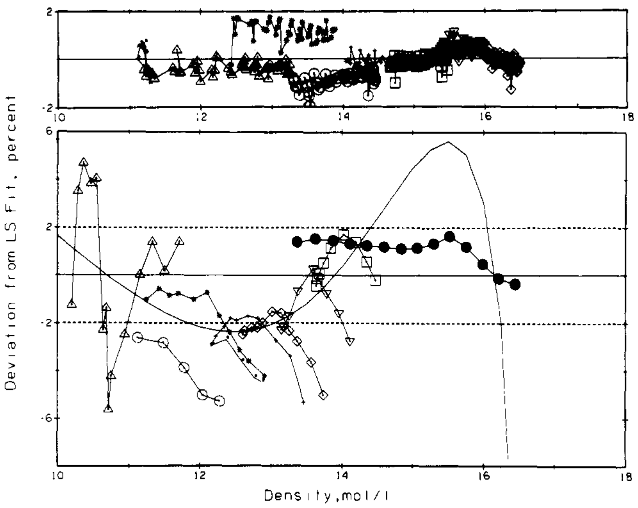

Figure 2. Deviations between experimental thermal conductivities and the calculated surface. Upper part, isotherms of this paper: (• and △) 299, (*) 260, (○) 227, (+) 196, (□) 169, (▽) 139, and (◇) 111 K. Lower part, ref *1-5*: (△) 323.15 K, ref *1*; (□) 212.90, (▽) 232.70, (◇) 253.20, (+) 267.70, and (*) 298.20, ref *2*; (•) 277.59 and (○) 310.93 K, ref *3*; (●) saturated liquid, 93–223 K, ref *4*; (—) saturated liquid, 90–302 K, old correlation, ref *5*.

at their lowest temperature, 323 K, which is some 30 K above our highest temperature. The isotherms in ref *2* when plotted in the thermal conductivity–density plane occasionally cross each other. In addition, several of the isotherms are not smooth but show distinct uncharacteristic "humps". This behavior can be seen in Figure 2. Half of the points in ref *3* are at 311 K, that is, slightly above our highest temperature. The agreement between the new values and those of ref *4* is excellent. The values in ref *4* are given for the saturated liquid. Our values for the saturated liquid are obtained from the overall surface fit. For the old correlation (ref *5*) only the departures at the saturation boundary are shown. Since this correlation is based on ref *1*–*4* among others, it is not surprising that the deviations seen here are a composite of those in the remainder of the comparison. Not shown in Figure 2 are the departures of the old model (ref *5*) from the new data or the new model for the compressed liquid states. The departures between old and new models increase as the density or pressure increases; they also increase as the temperature decreases. The maximum difference is 30% at 111 K and 16.5 mol/L with the values predicted by the model of ref *5* being higher than those of the new one.

Conclusion

The thermal conductivity of liquid propane has been measured for temperatures from 110 to 300 K and with pressures up to 70 MPa. The estimated uncertainty in the thermal conductivity is ±1.5%, the main source of uncertainty being the absence of the radiative heat transfer correction. The results can be represented with an equation for the thermal-conductivity surface and have been used to improve this correlation at low temperatures and high densities.

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Supplementary Material Available: The complete Table I covering 400 experimental points (8 pages). Ordering information is given on any current masthead page.