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Liquid Thermal Conductivities of Organic Compounds and Petroleum Fractions

GEORGE M. MALLAN,[1] MARSHALL S. MICHAELIAN,[2] and FRANK J. LOCKHART[3]
Department of Chemical Engineering, University of Southern California, Los Angeles, Calif. 90007

Liquid thermal conductivities of 29 organic compounds and 15 petroleum fractions have been measured in a transient, relative apparatus of the hot wire type between 20° and 120°C at a pressure of 7.5 atm.

Liquid thermal conductivity is a physical property difficult to measure accurately. Natural convection caused by the imposed temperature difference tends to make experimental values too high. It is known now that many data in reference books and handbooks are in error on the high side by 20% or more.

Of all organic compounds, toluene has been the one studied most for thermal conductivity. It is instructive to note how the experimental values of *k* have changed over the past 40-odd years, as shown in Table I. The decrease is due to improvements in instrumentation and experimental techniques. Figure 1 shows the data graphically and emphasizes that at the present time there is no assurance that future measurements will not give even lower values. Thermal conductivity measurements for other organic compounds show similar variations over the years.

This paper reports thermal conductivities of 29 organic compounds and 15 petroleum fractions as a function of temperature, determined experimentally in relative, transient equipment.

Table I. Thermal Conductivity of Liquid Toluene at 20°C

Year	Observers	Method[a]	*k*, *W/m* °C
1923	Bridgman (*2*)	CSA	0.1547
1924	Rice (*14*)	CSR	0.1414
1930	Smith (*19*)	CSA	0.1488
1931	Shiba (*18*)	PIEZO	0.1469
1934	Kardos (*11*)	WSR	0.1450
1949	Abas-Zade (*1*)	WSA	0.1395
1951	Riedel (*15*)	C-P-S, SA	0.1360
1954	Schmidt, Leidenfrost (*17*)	CSA	0.1362
1956	Challoner, Powell (*4*)	PSA	0.1378
1956	Frontasev (*5*)	PSA	0.1364
1957	Vargaftik (*21*)	WSA	0.1347
1957	Briggs (*3*)	CSR	0.1364
1959	McCready (*12*)	CSA	0.1386
1959	Frontasev, Gusakov (*6*)	PSA	0.1359
1961	Ziebland (*23*)	CSA	0.1343
1963	Jamieson, Tudhope (*9*)	WSA	0.1338
1963	Horrocks, McLaughlin (*8*)	WTA	0.1345
1965	Venart (*22*)	CSA	0.1327
1967	Poltz, Jugel (*13*)	PSA	0.1306

[a] Method:
C = cylinders
W = wire
P = plates
S = spheres
S = steady state
T = transient
A = absolute
R = relative

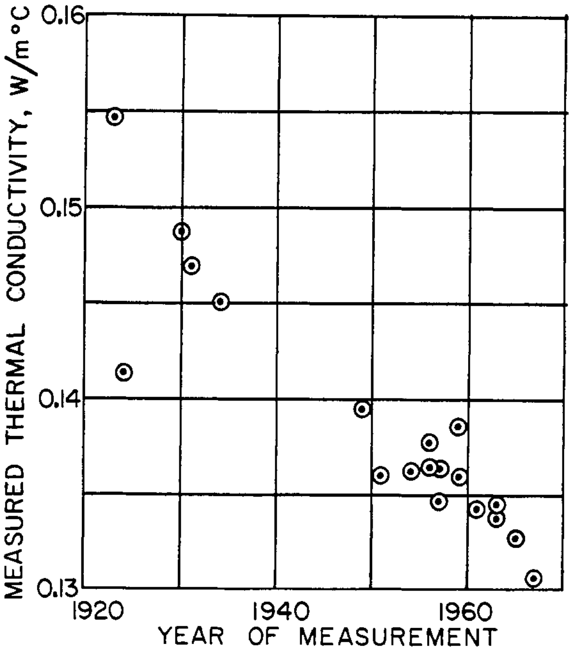

Figure 1. Thermal conductivity at 20°C of liquid toluene

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[1] Present address, Garrett Research and Development Co., Inc., La Verne, Calif.
[2] Present address, Chevron Research Corp., Richmond, Calif.
[3] To whom correspondence should be addressed.

APPARATUS

A comparative-type transient hot wire apparatus was used for data collection for two reasons: the speed of measurement and the ability readily to detect the onset of natural convection. The concept for the transient hot wire method for measuring thermal conductivity was suggested about 40 years ago, but was not fully exploited due to difficulties in techniques. The first satisfactory absolute determination by a transient apparatus was conducted by Horrocks and McLaughlin (*8*). A far simpler comparative method was demonstrated by Grassmann and Straumann (*7*)—a slightly modified copy of their device was used for the collection of the experimental data contained herein. More recently Tauscher (*20*) used a similar device.

In the transient operation of the hot wire apparatus, a constant electrical current is passed through a thin wire suspended vertically within a liquid medium initially in thermal equilibrium with its surroundings. As the wire temperature increases owing to its electrical resistance, it loses heat by conduction into the surrounding liquid. After a very brief induction period of about $^1/_{10}$ of a second, the heat transfer rate from the wire source into the liquid becomes constant provided that: (1) the surrounding liquid is large enough to absorb all the heat transferred and still retain its initial equilibrium temperature at some point removed from the heat source; (2) the physical properties of the liquid do not change appreciably owing to the absorption of the heat. Both of these provisions are relatively easy to meet since the duration of the transient operation is about 4–10 sec and the temperature increase in the wire itself is only about 1–3°C. In the comparative approach used herein, the temperature response of the hot wire immersed in the liquid of known thermal conductivity was compared with the corresponding response of the same wire immersed in the test liquid. The temperature change is recorded as a function of the change of resistance of the hot wire on an *X-Y* plotter as a logarithmic function of time, thereby generating a linear plot of the data. The circuit diagram for the apparatus is shown in Figure 2, and the component list is given in Table II. A more detailed diagram of the identical *X* and *Y* cells is shown in Figure 3.

In the operation of this apparatus, reagent grade toluene was used as the standard. The thermal conductivity data as reported by Ziebland (*23*) were used as the reference. In actual operation, the *Y* cell of the circuit is first filled with the calibration liquid toluene and the *X* cell with any liquid of relatively high viscosity. This property is necessary to ensure that the *X* cell will not become limiting with respect to the onset of natural convection. Once a *Y* cell calibration has been obtained, the liquid in the *X* cell is not changed and its temperature must remain constant. During operation, the *X* cell was maintained at a constant temperature of about 40°C while the *Y* cell was varied from 20–120°C at pressures up to $7^1/_2$ atmospheres. With toluene in the *Y* cell, a cell constant is obtained by multiplying the slope obtained from the *X-Y* plotter times the thermal conductivity of toluene as reported at that tempera-

Table II. Components in Circuit Diagram

R1	Measuring hot wire elements; 1-mil diameter iridium wire 6 in. long. Approx. 28 Ω
R2	2000 Ω, metal film resistors
R3	3000 Ω, metal film resistors
R_x4a	Constantan wire in constant temp bath, (26.5) Ω
R_x4b	Variable Helipot, 0–500 Ω
R_y4a	Constantan wire in constant temp bath with 14 center taps (24–34) Ω
R_y4b	Variable Helipot, 0–1000 Ω
R5	1200 Ω, carbon resistors
R6	900 Ω, carbon resistor
S1	Main circuit switch
S2	Shunt switch for passing feeble current to bridge circuits
S3	Balance power switch
S4	Shunt switch for balancing power supplies
S5	Two switches for balancing *x* and *y* Wheatstone bridge circuits
S6	Record switch
P_x, P_y	Regulated dc power supplies, 0–36 V, 0–$1^1/_2$ amp (operated at 2.8 V)
X-Y recorder	Moseley Model 7000A (operated at a sensitivity of 0.2 mV/in.)
Microvoltmeter	Hewlett-Packard Model 425A (used for balancing the bridge circuits) (operated at a sensitivity of 0.1 mV)

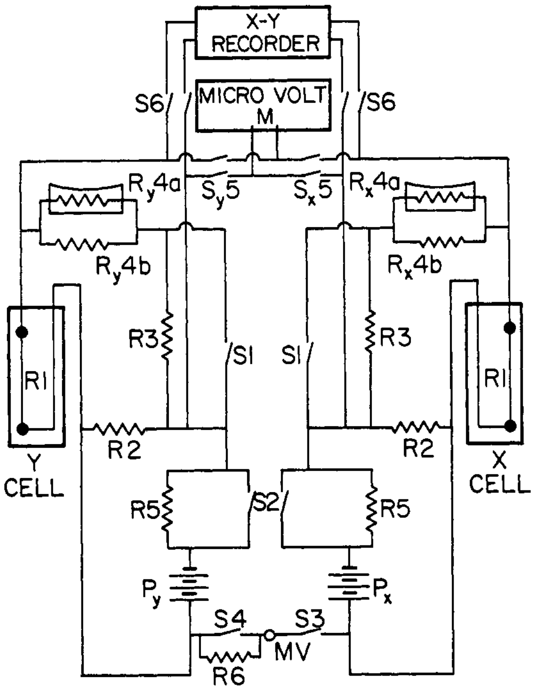

Figure 2. Circuit diagram for transient hot-wire apparatus

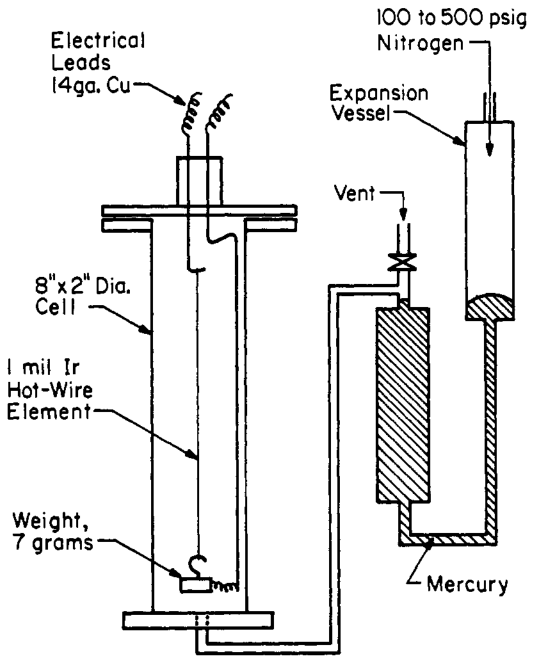

Figure 3. Thermal conductivity cell and pressurizing system

ture by Ziebland. Cell constants are thus obtained as a function of temperature throughout the range of interest. The thermal conductivity at temperature t of any new unknown liquid in the Y cell is then obtained by dividing this constant at temperature t with the slope obtained from the X-Y plotter.

OPERATION

Ten repetitive runs (each run lasting less than 10 sec) at 1- or 2-min intervals were recorded at each temperature level to establish an average value for the linear portions of the X-Y recorder slopes. The 95% confidence limit of each set of 10 slopes is approximately ±0.65%. Inasmuch as the ratio of two slopes is involved, the relative thermal conductivity should have a 95% confidence limit of about ±1.3%.

Experimental data were obtained for usually at least two samples for each liquid. Runs were made at cell pressures of about 7.5 atm. Comparisons were made with data for some liquids at 1.0 atm and no discernible differences were detected.

EXPERIMENTAL

The original data (complete tables of 29 organic compounds and 26 petroleum fractions) have been deposited with the American Chemical Society Microfilm Depository Service. They have not been corrected for absorptivity, as for example, suggested by Poltz and Jugel (*13*).

Tables III and IV present the equations for liquid thermal conductivity calculated from the experimental data on 29 organic compounds and 15 petroleum fractions. If we consider

Table III. Thermal Conductivities of Organic Compounds

$k = A - Bt$, k in W/m °C, t in °C

Compounds 1-8, pure grade; 24 technical grade; all others reagent grade

Liquid	No. of temp levels	Temp range, °C	Thermal conductivity		
			A	B (10^3)	Std dev
n-Pentane	6	26–106	0.1238	0.343	0.0011
n-Hexane	18	23–93	0.1267	0.312	0.0009
n-Heptane	18	25–86	0.1279	0.227	0.0009
n-Octane	9	25–97	0.1387	0.349	0.0012
n-Nonane	5	29–118	0.1378	0.318	0.0008
n-Decane	23	29–121	0.1407	0.274	0.0008
n-Dodecane	7	21–132	0.1414	0.290	0.0007
Methylcyclohexane	21	28–120	0.1172	0.243	0.0007
Benzene	7	30–126	0.1420	0.246	0.0009
p-Xylene	10	26–111	0.1407	0.337	0.0017
Methanol	5	23–89	0.1890	0.608	0.0045
Ethanol	12	23–120	0.1761	0.330	0.0010
1-Propanol	6	23–108	0.1610	0.299	0.0007
2-Propanol	6	23–108	0.1416	0.240	0.0004
1-Butanol	7	21–127	0.1525	0.243	0.0014
2-Butanol	5	21–127	0.1398	0.240	0.0004
Cyclohexanol	24	25–109	0.1382	0.153	0.0007
Propylene glycol	38	18–98	0.2028	0.084	0.0017
1,3-Butanediol	24	18–102	0.1968	0.483	0.0020
1,4-Butanediol	26	18–102	0.2179	0.274	0.0023
Butyraldehyde	17	25–109	0.1460	0.237	0.0014
Acetone	7	25–111	0.1716	0.508	0.0018
2-Nitropropane	18	27–112	0.1453	0.318	0.0011
Nitrobenzene	20	26–110	0.1535	0.221	0.0010
m-Nitrotoluene	27	23–121	0.1438	0.184	0.0009
Benzonitrile	20	25–110	0.1546	0.243	0.0012
N,*N*-Dimethylacetamide	20	25–110	0.1772	0.399	0.0017
Carbon tetrachloride	14	25–92	0.1055	0.209	0.0006
Tetrachloroethylene	12	25–74	0.1132	0.221	0.0020

Table IV. Thermal Conductivities of Liquid Petroleum Fractions

$k = A - Bt$, k in W/m °C, t in °C

Oil	°API	Viscosity, cP			Characterization factor, K	No. of temp. levels	Temp. range, °C	Thermal conductivity		
		25°C	50°C	98.8°C				A	B (10^3)	Std dev
2	43.9	0.8	0.8	0.8	11.3	6	22–127	0.1272	0.312	0.0019
3	21.7	39	18.8	4.4	11.3	8	25–155	0.1214	0.187	0.0007
4	30.2	4.5	2.9	1.0	11.5	6	22–115	0.1187	0.175	0.0012
6	43.8	1.5	1.1	0.9	11.9	4	22–115	0.1222	0.190	0.0006
7	22.4	190	50	8.5	11.8	11	25–155	0.1282	0.150	0.0019
8	29.8	9.4	6.1	2.2	11.8	10	25–139	0.1281	0.215	0.0016
9	50.2	0.8	0.8	0.8	11.4	7	22–127	0.1292	0.340	0.0018
10	33.9	4.5	3.2	1.3	11.7	9	26–121	0.1260	0.246	0.0016
11	16.7	2.1	1.1	0.8	10.1	5	30–115	0.1354	0.212	0.0005
21	41.6	2.3	1.5	0.8	12.0	21	25–121	0.1292	0.190	1.0005
22	33.7	4.7	2.5	1.2	12.0	6	32–119	0.1201	0.087	0.0049
23	40.4	5.3	2.9	1.3	12.0	14	30–120	0.1397	0.196	0.0004
24	28.4	235	64	12.4	12.4	23	27–106	0.1491	0.137	0.0006
25	25.6	2500	430	48	12.3	12	32–120	0.1620	0.125	0.0004
26	28.9	10,000	1500	150	12.6	15	24–121	0.1160	0.009	0.0004

the accuracy of the relative measurements given above and the reported accuracy (better than 1%) of Ziebland's equation for the k of toluene (*23*), the values of Tables III and IV are considered accurate to within about 2.5%. Any future changes in the k of toluene can be used to correct the k values reported here.

The apparatus and experimental measurements have been validated by comparing the values of k of a number of compounds at 20°C and B, the temperature coefficient of thermal conductivity, with values as evaluated by Jamieson and Tudhope (*10*) to be accurate to within ±2%. For example, the values of k at 20°C agree to within about 1.5% for ethanol and carbon tetrachloride. The values of B reported (*10*) vary considerably, but the present values fall within their range.

Each petroleum fraction is identified further by experimental viscosity–temperature data and the specific gravity at 15.5°C. Limited data indicate that the density-temperature relationship can be represented satisfactorily by the nomograph of Ritter et al. (*16*). The characterization factor "K" is commonly used in the petroleum industry as an index of the paraffinicity of various oils. It is defined as the ratio of the cube root of the average boiling point (°R) at atmospheric pressure to the specific gravity at 60°F.

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Vapor Pressures Over NdI_3 and PrI_3

CHIKARA HIRAYAMA[1] and FLOYD E. CAMP
Westinghouse Research Laboratories, Pittsburgh, Pa. 15235

The sublimation pressures of neodymium and praseodymium triiodides have been measured. The heats of sublimation, $\Delta H_{S_{298}}^\circ$, for NdI_3 and PrI_3 are 77.8 ± 0.6 and 78.6 ± 1.5 kcal/mol, respectively.

Except for samarium, europium, ytterbium, and lutetium, the trivalent salt is the normally stable state for the lanthanides. The divalent salt is the normally stable state for the former four lanthanides. It has been reported by Hastie et al. (*7*), that $EuCl_3$ and $LuCl_3$, for example, would be stabilized only by mixing these lanthanide salts with KCl.

The solid trihalides of the lanthanides, except those of Sm, Eu, Yb, and Lu, are generally believed to vaporize as the monomeric lanthanide trihalide. The trihalides of Sm, Eu, Yb, and Lu are known to disproportionate to the dihalide and the halogen gas. Mass spectrometric evidences have been obtained for a number of stable trifluorides (*17*) and trichlorides (*7*), and also over some stable dichlorides and dibromides (*6, 7*). Extensive vapor pressure measurements over the liquid trichlorides and dichlorides of the lanthanides have been reported by Russian workers (*12*). Some vapor pressure measurements over solid halides have also been reported (*13*). However, there has been a paucity of data on the vapor pressures over the lanthanide iodides. Shimazaki and Niwa (*13*) reported the vapor pressures over solid LaI_3, PrI_3, and NdI_3. These workers, however, did their measurements using fused silica torsion effusion cells. It is known that the lanthanide halides react with fused silica.

We here report the vapor pressures over solid NdI_3 and PrI_3 using tantalum effusion cells to compare against the results of Shimazaki and Niwa. This metal is nonreactive with the lanthanide iodides in the temperature range measured. Subsequently, we will report on the mass spectra over these iodides (*8*).

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[1] To whom correspondence should be addressed.