Thermal Conductivity Measurements
of Complex Saturated Hydrocarbons

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Thermal conductivities of complex saturated hydrocarbons were measured from 145° to 316° F. Major hydrocarbon groups investigated were cyclohexanes, bicyclohexyls, tercyclohexyls, decalins, and hydrindans. A hot-wire method was used, and, in some instances, results using this apparatus were compared with those obtained by instruments of three other basic types—disk, cylinder, and sphere. For seven determinations of diethylcyclohexane at 145° F., the relative standard deviation was 1.9% using the hot-wire technique.

IN THE PAST DECADE, several comprehensive reviews have reported the measurement of thermal conductivity of fluids by instruments of four basic types—disk, cylinder, sphere, and hot-wire. Sakiadis and Coates (17) set up an arbitrary "rating scale" to evaluate the work and the reliability of the results of many investigators based on accuracy of measurement of the dimensions of the apparatus, accuracy of temperature measurements, heat losses, and consistency of data.

As noted by other authors (5), "thermal conductivity of liquids has been characterized by both scarity and discrepancies" in the literature. The values reported by different investigators for the same substance using similar experimental equipment are often ambiguous and inconsistent. Furthermore, data listed in chemical handbooks are meager and unsubstantiated as to origin and accuracy. Therefore, during the course of these experimental investigations, a literature search was undertaken by the authors to determine the "best" values of thermal conductivity for specific compounds and the type of instrumentation used for these analyses. With this basic knowledge, the results obtained with the hot-wire method were compared with those from other instruments. This article summaries experimentally determined thermal conductivity measurements for many new complex saturated hydrocarbons.

EXPERIMENTAL

The hot-wire technique was chosen for the thermal conductivity measurements of hydrocarbons. The cell (Figure 1) developed by Cecil and Munch (5) is designed to place thermal conductivity results on an absolute basis using small samples of liquid (~20 ml.). For measurements at elevated temperatures, the thermal conductivity cell is
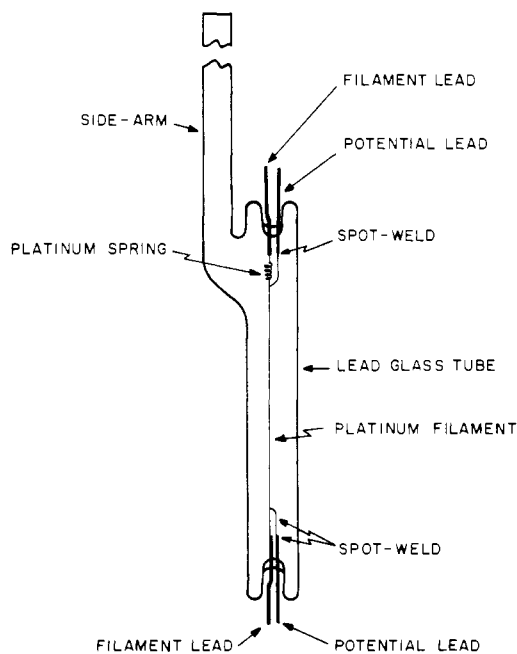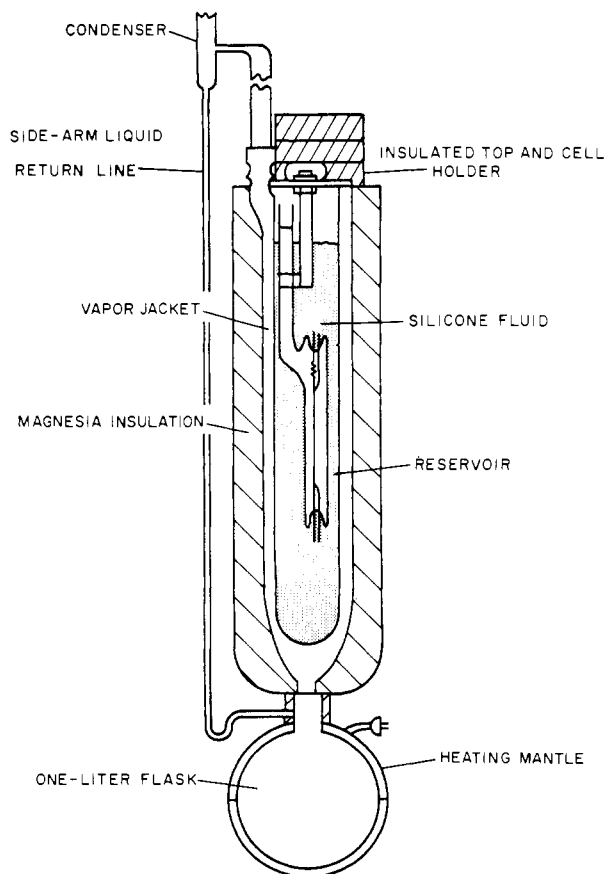

Figure 1. Hot-wire thermal conductivity cell

Figure 2. Schematic of thermostatically controlled silicone fluid bath

Temp., °C.	$K \times 10^{-5}$ (Cal./Cm. °C. Sec.) Found	$K \times 10^{-5}$ (Cal./Cm. °C. Sec.) Literature	% of Lit. Value	Temp., °C.	$K \times 10^{-5}$ (Cal./Cm. °C. Sec.) Found	$K \times 10^{-5}$ (Cal./Cm. °C. Sec.) Literature	% of Lit. Value
		Aroclor 1248[a]				OS-45[a]	
63	23.4	23.3 (5) -23.4 (14)E[b]	100.6	104	29.7	30.9 (4)E	96.3
63	23.4	23.3	100.6	104	30.7	30.9	99.6
104	23.3	22.9 (14)E	101.4	104	29.7	30.9	96.2
104	23.4	22.9	102.0	158	29.2	28.3 (4)E	102.9
158	23.9	22.4 (14)E	106.5	158	28.6	28.3	101.0
158	23.0	22.4	102.8	158	28.5	28.3	100.5
158	23.6	22.4	105.4	158	28.7	28.3	101.4
158	23.4	22.4	104.5			Dibutyl Phthalate	
		Tricresyl Phosphate		63	32.0	30.8 (5)E	103.8
63	29.4	31.3 (4)E	94.1	63	31.6	30.8	102.7
63	29.8	31.3	95.3				
63	30.0	31.3	95.8			Dioctyl Phthalate	
63	29.9	31.3	95.5	63	30.3	31.4 (5)E	96.6
104	29.2	30.1 (4)E	97.1	63	30.7	31.4	97.7
104	29.0	30.1	96.3			Dowtherm "A"[c]	
158	28.5	28.1 (4)E	101.3	63	30.5	32.7 (4)E	93.2
158	27.7	28.1	98.5	63	31.0	32.7	94.7
		OS-45[a]		104	30.2	32.1 (4)E	94.1
63	30.2	32.6 (4)E	92.7	104	30.6	32.1	95.5
63	30.4	32.6	93.3	104	30.3	32.1	94.5

[a] Registered trademark of Monsanto Chemical Co. [b] E = Extrapolated from reported data and curves. [c] Dow Chemical Co. trademark.

immersed in a thermostatic silicone fluid bath (Figure 2), the temperature of which is maintained by a condensing vapor bath. This bath assembly, with slight modifications, is another design of Munch, Cecil, and Koerner (4).

To maintain the vapor bath at a constant, reproducible temperature, the outlet of the condenser is fitted with a glass tee, one end of which is connected to a mercury manometer, the other to a vacuum line. A fixed pressure setting is maintained by monitoring the mercury level in the manometer with a sensing device attached to an electronic controller which, in turn, regulates the operation of an electronic valve located in the vacuum line. Any rise in mercury level is immediately sensed and causes the electronic valve to open automatically to vacuum until the mercury level is brought back to its pre-set height. Using this type of pressure control, temperature differences were regulated to within ±0.002° C.

The cell constants were calculated from the dimensions of the various components of the cell assembly (5). The apparatus was then evaluated by determining the thermal conductivity of compounds (4, 5) at 63° C., 104° C., and 158° C. These results are compared with those of other analysts in Table I. Although variations between results do exist, it is very probable that these differences can be attributed to impurities and composition changes in the commercial products and to differences in the length of time selected by various investigators for establishing steady-state measurements at various currents to give a series of ΔT values for corresponding values of power input, RI^2. Complete details concerning the construction and theoretical aspects of this cell and bath design are available (4, 5).

RESULTS

A comparison of the results of the present work and of literature measurements for specific compounds is presented in Table II. The type of test equipment used for the determination of these values is noted. The average value obtained in the present work divided by that of other analysts at 63° C. is indicated as a percentage in the last column.

Although the values derived by hot-wire techniques are consistent (Table I), they are in some instances about 10% lower than those reported using a cylindrical apparatus. This is not true for glycerol, o-xylene, and toluene. Cecil and Munch (5) also found low values for Arochlor 1248 at 63° C. as compared with data obtained from a cylindrical apparatus (22). The results for glycerol determined by Bates (1) and Kaye (10) using, disk-type instruments and the results of Riedel (16) for o-xylene and chlorobenzene using a spherical apparatus are essentially the same as the authors. The good agreement (Table II) between our data and those derived by cylindrical, disk, and spherical instrumentation show that the hot-wire method is valid and accurate.

Recent investigations by Monsanto personnel have shown that, at temperatures of 175° C. or higher, a significant amount of convection occurs in the oil bath thereby inducing convection in the sample cell. This results in heat transfer from the center filament by a combination of conduction and convection; consequently erroneous high thermal conductivity values would be obtained since all of the heat transfer would be attributed to conduction in the subsequent calculation. This phenomena was not observed in our slightly modified apparatus over the temperature range of 63° to 158° C.

The thermal conductivity values for the hydrocarbon fuels investigated with the apparatus and procedure adopted for this study are listed in Table III. For seven determinations of diethylcyclohexane at 145° F., the relative standard deviation was 1.9%.

Purity of the hydrocarbons cited in Table III was established by gas-liquid chromatography and is reported in the literature by Belenyessy and coauthors (2) who also determined the heats of combustion for many of these compounds. Furthermore, Gudzinowicz, Campbell, and Adams (7) recently reported the heat capacities for these compounds.

Table II. Thermal Conductivity Measurements of Select Organic Compounds

Method[a]	Temp., °C.	Thermal Conductivity $K \times 10$ (Cal./Cm. °C. Sec.)	Comparison of Results, %
		Glycerol	
HW	63	68.8	...
HW	63	68.8 } 68.8[b] (av.)	...
C	63	74.1 (18)E[c]	92.9
C	63	70.2 (11)E	98.0
C	63	72.5 (13)E	94.8
D	63	67.8 (1)E	101.4
D	63	69.4 (10)E	99.1
S	20	68.6 (15)	...
C	20	68.0 (3)	...
C	63	66.8 (22)	103.0
		o-Xylene	
HW	63	29.4	...
HW	63	29.4 } 29.4[b] (av.)	...
...	−20 to +80	34.1 (9)	...
...	0	34.4 (8)	...
...	33	25.2 (8)	...
...	20	37.2 (6)	...
S	63	29.8 (16)E	98.6
C	20	32.5 (3)	...
		Toluene	
HW	63	28.7	...
HW	63	28.9 } 28.8[b] (av.)	...
...	20	32.2 (9)	...
...	80	28.1 (9)	...
...	0	34.9 (8)	...
...	12	30.7 (8)	...
...	30	35.5 (6)	...
...	75	34.7 (6)	...
S	63	29.4 (16)E	97.9
C	63	30.8 (11)E	93.4
C	20	32.6 (3)	...
		Aroclor 1248[d]	
HW	63	23.4	...
HW	63	23.4 } 23.4[b] (av.)	...
...	30 to 100	28.1 (9)	...
HW	63	23.3 (5)E	100.6
C	63	28.4 (20)E	82.4
C	63	26.9 (22)E	87.0
HW	20	23.7 (12)	...
C	20	27.6 (21)	...
		n-Decane	
HW	63	29.0	...
HW	63	28.4 } 28.7[b] (av.)	...
C	63	31.9 (20)E	...
C	63	31.6 (17)E	90.9
C	20	34.0 (3)	...
		n-Nonane	
HW	63	28.4	...
HW	63	28.1 } 28.2[b] (av.)	...
...	30–100	33.7 (9)	...
...	30	34.7 (6)	...
C	63	31.9 (17)E	88.6
C	63	32.6 (20)E	86.7
		Chlorobenzene	
HW	63	28.0	...
HW	63	27.7 } 27.9[b] (av.)	...
...	30 to 100	34.6 (9)	...
...	12	30.2 (8)	...
...	10	34.3 (6)	...
S	63	28.6 (16)E	97.6
...	30	32.1 (19)	...
C	63	33.4 (20)E	83.5
		Nitrobenzene	
HW	63	32.9	...
HW	63	32.5 } 32.7[b] (av.)	...
...	30 to 100	39.1	...
...	12.5	38.0 (8)	...
C	63	38.0 (20)E	86.1
S	20	36.2 (15)	...

[a] HW = Hot Wire, C = Cylinder, D = Disk, S = Sphere. [b] Monsanto Research Corp. values. [c] E = Extrapolated or calculated from data reported. [d] Registered trademark of Monsanto Chemical Co.

Table III. Thermal Conductivity Data for Hydrocarbon Fuels

K [B.t.u./Hr. Ft.^{2} (° F./Ft.)]

	145° F.	219° F.	316° F.
Cyclohexanes			
Diethylcyclohexane	0.060(7)[a]	0.059(6)	...
Hexaethylcyclohexane	0.065(4)	0.063(4)	...
tert-Butylcyclohexane	0.056(2)	0.059(2)	...
Bis-(cyclohexylmethyl)-cyclohexane	0.064(2)	0.066(2)	...
Bicyclohexyls			
Bicyclohexyl	0.062(2)	0.061(2)	...
2-Ethylbicyclohexyl	0.063(2)	...	...
Isopropylbicyclohexyl	0.061(6)	0.060(4)	0.059(6)
Cyclopentylbicyclohexyl	0.066(2)	0.063(2)	0.063(2)
4-n-Heptylbicyclohexyl	0.071(5)	0.067(4)	0.065(2)
4-n-Nonylbicyclohexyl	0.070(9)	0.071(4)	...
Tercyclohexyls			
o-Tercyclohexyl	0.063(3)	0.062(4)	...
4-n-Heptyltercyclohexyl	0.065(2)	0.063(5)	...
Decalins			
Decalin	0.062(7)	0.061(4)	0.059(4)
α-Methyldecalin	0.056(2)	0.062(2)	...
β-Methyldecalin	0.056(2)	0.058(2)	...
Dimethyldecalin	0.059(2)	0.057(2)	0.056(2)
Dimethanodecalin	0.063(7)	0.063(4)	0.061(6)
α-Ethyldecalin	0.058(2)	0.063(3)	...
β-Ethyldecalin	0.057(2)	0.059(4)	...
Ethyldecalin	0.059(2)	...	...
α-n-Propyldecalin	0.057(3)	0.062(2)	...
α-Isopropyldecalin	0.059(2)	0.059(2)	...
Isopropyldecalin	0.060(2)	0.058(2)	0.057(2)
α-n-Butyldecalin	0.061(2)	0.061(3)	...
α-sec-Butyldecalin	0.057(2)	0.059(2)	...
α-Isobutyldecalin	0.060(3)	0.060(2)	...
tert-Butyldecalin	0.057(2)	0.056(2)	0.056(2)
Hydrindans			
Hydrindan	0.067(2)	0.064(3)	...
Methylhydrindan	0.061(2)	0.059(2)	0.059(2)
Ethylhydrindan	0.061(2)	0.060(2)	0.060(2)
Isopropylhydrindan	0.061(2)	0.059(2)	0.059(2)
1-Cyclohexyl-3-methylhydrindan	0.062(2)	0.060(2)	...
1-Cyclohexyl-1,3,3-trimethyl-hydrindan	0.057(2)	0.058(2)	0.057(2)
Miscellaneous Structures			
Dicyclohexylmethane	0.065(2)	0.062(2)	0.062(2)
Bis(2,4,6-trimethylcyclohexyl)-methane	0.059(2)	0.059(2)	...
Cyclohexyl(ethylcyclohexyl)-methane	0.063(2)	0.060(2)	0.060(2)
Bis(ethylcyclohexyl)methane	0.062(2)	...	...
Cyclohexyl(isopropylcyclohexyl)-methane	0.062(2)	0.062(2)	...
1,1-Dicyclohexylethane	0.064(2)	0.062(2)	0.060(2)
1,2-Dicyclohexylethane	0.065(2)	0.065(2)	...
1,1-Bis(dimethylcyclohexyl)-ethane	0.061(2)	0.058(2)	0.058(2)
1,1-Bis(ethylcyclohexyl)ethane	0.067(2)	0.064(2)	0.061(2)
1-Cyclohexyl-1-isopropyl-cyclohexylethane	0.061(2)	0.061(2)	0.060(2)
1,2-Dicyclhexylpropane	0.065(2)	...	...
1,1,3-Tricyclohexylpropane	0.064(2)	...	...
1,3-Dicyclohexylbutane	0.066(2)	0.063(2)	...
1,1-Dicyclohexylheptane	0.069(2)	0.066(2)	...
Bicyclopentyl with 0.01% cyclopentyl bromide	0.068(2)	0.063(2)	...
Bicyclopentyl with 0.10% cyclopentyl bromide	0.069(2)	0.064(2)	...
1,3-Dicyclopentylcyclopentane	0.067(2)	0.068(2)	...
Perhydrophenanthrene	0.060(2)	0.060(2)	...
2-Ethylperhydrophenanthrene	0.061(3)	0.059(2)	...
Perhydromethylcyclo-pentadienedimer	0.060(2)	0.059(2)	...
Diethylperhydropyrene	0.057(2)	0.060(2)	...
9-Methylperhydrofluorene	0.062(2)	0.058(2)	0.058(2)
9-(2'-Ethylhexyl)perhydro-fluorene	0.063(2)	0.063(2)	...
Pinane	0.059(2)	0.057(2)	...

[a] Average of number of analyses performed shown in parentheses.

LITERATURE CITED

(1) Bates, K.O., *Ind. Eng. Chem.* 28, 494 (1936).
(2) Belenyessy, L.I., Gudzinowicz, B.J., Reid, R.C., Smith, J.O., J. CHEM. ENG. DATA 7, 66 (1962).
(3) Briggs, K.H., *Ind. Eng. Chem.* 49, 418 (1957).
(4) Cecil, O.B., Koerner, W.E., Munch, R.H., *Ind. Eng. Chem. Data Series* 2, 54 (1957).
(5) Cecil, O.B., Munch, R.H., *Ind. Eng. Chem.* 48, 437 (1956).
(6) Chemical Engineers' Handbook, J.H. Perry, ed., McGraw-Hill, New York, 1950.
(7) Gudzinowicz, B.J., Campbell, R.H., Adams, J.S., J. CHEM. ENG. DATA 8, 201 (1963).
(8) Handbook of Chemistry, N.A. Lange, Handbook Publishers, Sandusky, Ohio, 1956.
(9) Handbook of Chemistry and Physics, 39th ed., Chemical Rubber Publisher Co., Cleveland, Ohio, 1957.
(10) Kaye, G.W.C., Higgins, W.F., *Proc. Roy. Soc. (London)*, Ser. A. 117, 459 (1927).
(11) McCready, D.W., WADC Tech. Rept. 58-405, March, 1959.
(12) McNall, P.E., unpublished dissertation, Dept. of Mech. Eng., Purdue University, Lafayette, Ind., 1951.
(13) Mason, H.L., *Trans. A.S.M.E.* 76, 817 (1954).
(14) Monsanto Chemical Co., Organic Division, St. Louis, Mo., Monsanto Technical Report on Arochlor 1248, p. 3.
(15) Riedel, L., Mitt. Kaltestech. Inst. Reichstorsch. Anstalt Lebensmittelfreischalt tech. Hochschule, No. 2, 44p., Karlsruhe, 1947.
(16) Riedel, L., *Chem. Ingr.-Tech.* 23, 321 (1951).
(17) Sakiadis, B.C., Coates, J., Louisiana State Univ. Eng. Exp. Sta. Bull. No. 34 (1952).
(18) Sakiadis, B.C., Coates, J., *A.I.Ch.E.J.* 1, 275 (1955).
(19) Shiba, H., *Sci. Papers Phys., Chem. Research* 16, 205 (1931).
(20) Smith, J.F.D., *Trans. A.S.M.E.* 58, 719 (1936).
(21) Woolf, J.R., unpublished disseration, Dept. of Mechanical Engineering, Purdue University, Lafayette, Ind., 1951.
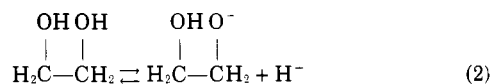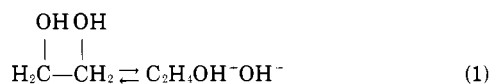(22) Woolf, J.R., Sibbitt, W.L., *Ind. Eng. Chem.* 46, 1947 (1954).

Autoprotolysis Constants of Ethylene Glycol and Propylene Glycol and Dissociation Constants of Some Acids and Bases in the Solvents at 30°C.

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Autoprotolysis constants (K_s) of ethylene glycol and propylene glycol were determined at 30°C. electometrically by using a cell of the type $H_2|$ MX, M-glycoxide, glycol | AgX-Ag without liquid junction. The pK_s values are found to be 15.60 and 16.76, respectively, for the two solvents. Thermodynamic dissociation constants of six uncharged carboxylic acids and 12 monopositively charged acids of the type BH^+ (conjugate to amine B) were determined in the two glycols at 30°C. by e.m.f. measurements on cells without liquid junction using hydrogen electrode and silver–silver halide electrode in suitable buffers. The corresponding dissociation constants of the conjugate bases have been calculated. The role of the solvent on acid-base equilibria has been discussed.
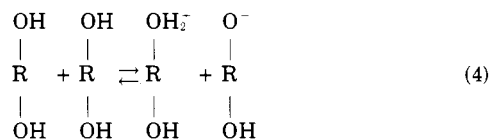
AUTOPROTOLYSIS. Like water and alcohols, glycols behave as amphiprotic solvents. Ethylene glycol is assumed to ionize in the following manner:

$$\begin{array}{cc} OH & OH \\ | & | \\ H_2C\!-\!CH_2 \end{array} \rightleftarrows C_2H_4OH^-OH^-$$ (1)

$$\begin{array}{ccccc} OH & OH & & OH & O^- \\ | & | & & | & | \\ H_2C\!-\!CH_2 & \rightleftarrows & H_2C\!-\!CH_2 + H^- \end{array}$$ (2)

The slow formation of chlorohydrin from glycol and hydrochloric acid as well as rapid formation of sodium-glycoxide from glycol and sodium metal is the chemical example for the above processes. The second stage of ionization of the glycol:

$$\begin{array}{cccc} OH & O^- & & O^- \;\; O^- \\ | & | & & | \quad | \\ H_2C\!-\!CH_2 & \rightleftarrows & H_2C\!-\!CH_2 + H^+ \end{array}$$ (3)
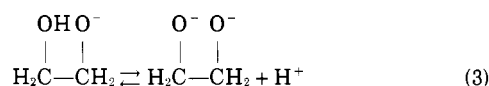
is a remote possibility. The ionization process represented by Equation 1 is presumably negligible and may occur in glycols (1) as:

$$\begin{array}{ccccccc} OH & & OH & & OH_2^+ & & O^- \\ | & & | & & | & & | \\ R & + & R & \rightleftarrows & R & + & R \\ | & & | & & | & & | \\ OH & & OH & & OH & & OH \end{array}$$ (4)

Representing the solvent molecule as SH and the ions as SH_2^+ and S^-, the autoprotolysis constant $K_S = a_{SH_2^+} \times a_{S^-}$, where "a" denotes activity.