Thermal Conductivity of Fluids. *n*-Decane

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The thermal conductivity of *n*-decane was measured at pressures up to 5000 p.s.i.a. and the temperature interval between 40° and 340° F. The experimental results are presented in tabular and graphical form. It was not possible to make comparisons of the thermal conductivity of *n*-decane with other investigators in either the gas or the liquid phase since earlier measurements of this quantity do not appear to be available.

EXPERIMENTAL information concerning the thermal conductivity of *n*-decane in the gas phase appears nonexistent, and only limited data are available for the liquid phase at atmospheric pressure (*2, 14, 17*). As a result of the paucity of information concerning thermal conductivity of *n*-decane, an experimental investigation of this quantity at pressures up to 5000 p.s.i.a. and the temperature interval between 40° and 340° F. was carried out. Measurements in the gas phase were limited to temperatures above 220° F. The effect of pressure on the thermal conductivity of *n*-decane in the liquid phase is much smaller than for the more volatile hydrocarbons. Therefore, fewer experimental measurements have been made than would have been required if the thermal conductivity had been a strong function of pressure.

EQUIPMENT AND METHOD

A conductivity cell of spherical configuration was employed in this experimental study (*10, 11, 12*). The equipment consists of a gold-plated sphere, 3.5 inches in diameter, concentrically located within a slightly larger spherical cavity yielding a radial transport path of approximately 0.020 inch between the inner sphere and the outer shell. An electric heater within the inner sphere was so located as to yield nearly equal thermal flux at all points around the spherical transport path. Small thermocouples of copper-constantan wire were employed to establish the temperature of the inner spherical surface and the inner surface of the outer shell. Appropriate corrections for the location of thermocouples within the stainless steel body of the shell and of the inner sphere were necessary (*10*).

Dimensions of the sphere and spherical cavity were established by direct mechanical measurements, and the over-all behavior of the instrument was checked periodically by measurements of the thermal conductivity of helium at atmospheric pressure (*5, 6, 7*). In the experimental program, measurements at each state were carried out at four different levels of thermal flux with a single exception. A period of approximately four hours was required to obtain steady state in the liquid phase and approximately eight hours in the gas phase.

The calculated value of the thermal conductivity at a measured value of the thermal flux is hereinafter called "apparent thermal conductivity." Gross convection within the spherical transport path was detected by rapid increases in the apparent thermal conductivity with the increase in the radial temperature gradient and from marked disparity between measurements made in the upper and lower hemispheres. Satisfactory agreement between the measurements in the upper and lower hemispheres was realized when gross convection was absent. Within the range of states and thermal gradients involved here, no indication of gross convection in the transport path was found. The variation in the apparent thermal conductivity with thermal flux is due in part to changes in the average temperature of the transport path and possibly to local regions involving convection at the higher fluxes.

Two sets of measurements were made with helium at atmospheric pressure in the course of this investigation. These measurements yielded values of 0.0904 and 0.0913 B.t.u. per (hour) (foot) (° F.) for a temperature of 130° F. These values are in good agreement with the critically chosen data of 0.0913 B.t.u. per (hour) (foot) (° F.) reported by Hilsenrath and Touloukian (*6*). Repeated flushing with helium was necessary to eliminate traces of gaseous *n*-decane. The presence of such traces of *n*-decane significantly decreased the measured thermal conductivity for helium.

MATERIALS

The *n*-decane employed in this investigation was obtained from the Phillips Petroleum Co. as research grade material with a reported purity of 0.9949 mole fraction *n*-decane. The sample of *n*-decane was refluxed for an extended period to remove traces of air, and the index of refraction of the air-free sample relative to the D lines of sodium was 1.4094 at 77° F. as compared with a value for an air-saturated sample of 1.40967 (*1*) for the same temperature. The *n*-decane in the liquid phase was dried by contact with metallic sodium. Apparently, the purity of the material was as reported, and the impurities were, for the most part, paraffin hydrocarbons containing 10 carbon atoms per molecule.

EXPERIMENTAL RESULTS

The influence of thermal flux upon the apparent thermal conductivity of *n*-decane at a temperature of 220° F. and a pressure of 2108 p.s.i.a. is shown in Figure 1. These

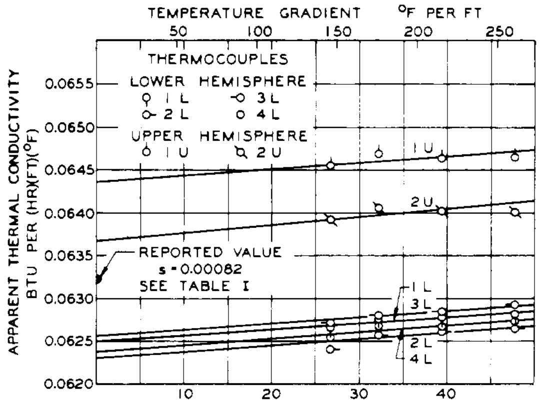

Figure 1. Effect of thermal flux upon apparent thermal conductivity at 2108 p.s.i.a. and 220° F.

values have been corrected for the individual position of the thermocouples relative to the surface of the inner sphere and the surface of the outer cavity. The variation in behavior in the upper and lower hemispheres was somewhat larger than methane (*3*) and much larger than *n*-butane (*4*). The behavior shown in Figure 1, with the values from the upper hemisphere being somewhat larger than those from the lower hemisphere, was typical of the results obtained throughout the investigation in the liquid phase. However, the effect of flux on the apparent thermal conductivity was even smaller than that reported for *n*-butane (*4*). The reported values of the apparent thermal conductivity for each thermocouple at zero flux were arrived at by least squares regression analysis for each thermocouple. Thus, the standard deviation applies to each straight line without the imposition of a single slope. The experimental results were subject to the analysis described earlier (*11*). The larger differences between the upper and lower hemispheres, shown in Figure 1, as compared with the earlier measurements, probably result from greater eccentricity of the inner sphere within the spherical cavity. The corrections (*11*) applied accounted for the radiant transfer between the spherical surfaces and the small thermal conduction along the stem supporting the inner sphere. The deviations of the experimental data from the upper and lower parts of the sphere were slightly larger at the higher pressures as a result of the greater eccentricity encountered in this region.

The experimental results are presented in Table I. Included are the number of experimental measurements involved for each state, the number of flux values investigated, the maximum flux, and the change in the flux per unit temperature difference. When there was a significant difference in this gradient, values for both the upper and lower hemispheres were tabulated. The standard error of estimate of experimental values from the straight line (Figure 1) is included, as well as the corrected values of the thermal conductivity, and the standard deviation of the area-weighted average of the apparent thermal conductivity at zero flux. A total of 14 states was investigated in the liquid phase and four states in the gas phase. A total of 71 observations was made of the apparent thermal conductivity distributed among the 18 states.

The thermal conductivity of *n*-decane in the liquid phase is shown as a function of pressure in Figure 2. Data for 160° and 280° F. have been interpolated, and the values for 400° F. have been obtained by extrapolation. As a result of the small change in thermal conductivity with pressure, a much smaller number of experimental points was required to establish thermal conductivity within the accuracy of experimental measurement than was necessary for methane (*3*) as an example. The limited data that were obtained

Table I. Experimental Conditions

Pressure, P.S.I.A.	Number Flux Values	Maximum Flux, B.t.u./Hr.	Number of Points	Gradient[a] ° F.$^{-1}$	Standard Error of Estimate[b] (B.t.u./Hr.)/(° F.)	Thermal Conductivity, B.t.u./(Hr.)(Ft.)(° F.)	Standard Deviation[c] B.t.u./(Hr.)(Ft.)(° F.)
				40° F.			
21	4	49.36	24	0.00415[d] −0.00343[e]	0.01741	0.075703	0.000404
4853	4	48.91	24	−0.00004	0.00782	0.080308	0.002123
				100° F.			
17	4	51.42	24	−0.00050[d] 0.00239[e]	0.00905	0.069730	0.000893
3079	4	46.77	24	−0.00005[d] −0.00166[e]	0.00829	0.074195	0.001913
5000	4	50.91	24	0.00051[d] −0.00249[e]	0.00850	0.076151	0.003349
				220° F.			
1.0	4	13.67	24	0.00607	0.00322	0.009043	0.000028
100	4	50.14	24	0.00053	0.00783	0.059792	0.000177
2108	4	47.61	24	0.00120	0.00675	0.063222	0.000821
4000	4	46.76	24	0.00020	0.00775	0.066056	0.001852
4900	4	47.14	24	0.00143[d] −0.00052[e]	0.01076	0.067044	0.002343
				280° F.			
1.0	3	9.84	18	0.01032	0.00256	0.010501	0.000021
				340° F.			
1.0	4	11.38	24	0.04150	0.01804	0.011430	0.000036
9.8	4	14.47	24	0.00555	0.00661	0.015156	0.000777
131	4	36.07	24	0.00100	0.00504	0.051882	0.000127
1063	4	36.56	24	0.00194	0.00583	0.053868	0.000301
2223	4	40.27	24	0.00121	0.00864	0.056390	0.000635
3856	4	43.83	24	0.00197	0.01254	0.058813	0.001393
4951	4	42.85	24	0.00337	0.01279	0.060171	0.001856

[a] Average value of gradient over all thermocouple measurements defined as: $d[(q_m/d\theta)/\Delta t_m]/d(q_m/d\theta)$.

[b] Standard error of estimate: $\sigma = \left\{\sum_1^N \left[\left(\frac{q_m/d\theta}{\Delta t_m}\right)_e - \left(\frac{q_m/d\theta}{\Delta t_m}\right)_s\right]^2/(N-1)\right\}^{1/2}$.

[c] Standard deviation from area-weighted average of the indications of the six thermocouples: $s = [\sum_1^N (k'_{av} - k')^2/N]^{1/2}$.

[d] Average value of gradient of thermocouples in lower hemisphere.

[e] Average value of gradient of thermocouples in upper hemisphere.

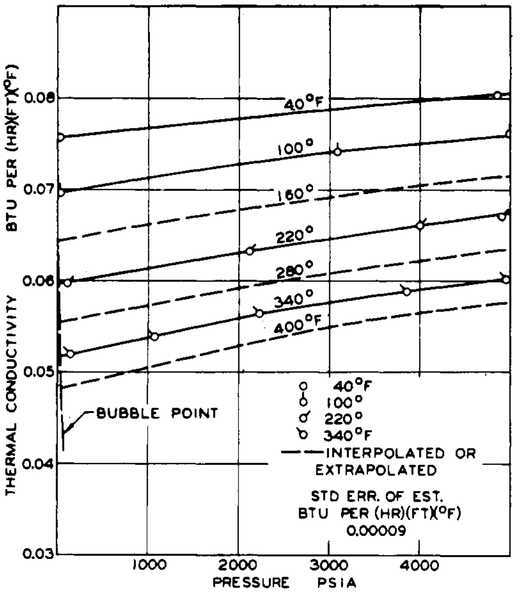

Figure 2. Thermal conductivity of *n*-decane in the liquid phase

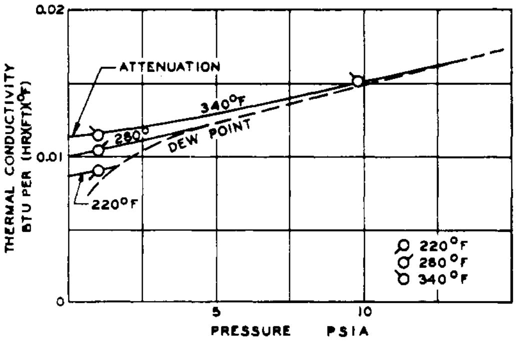

Figure 3. Thermal conductivity of *n*-decane in the gas phase

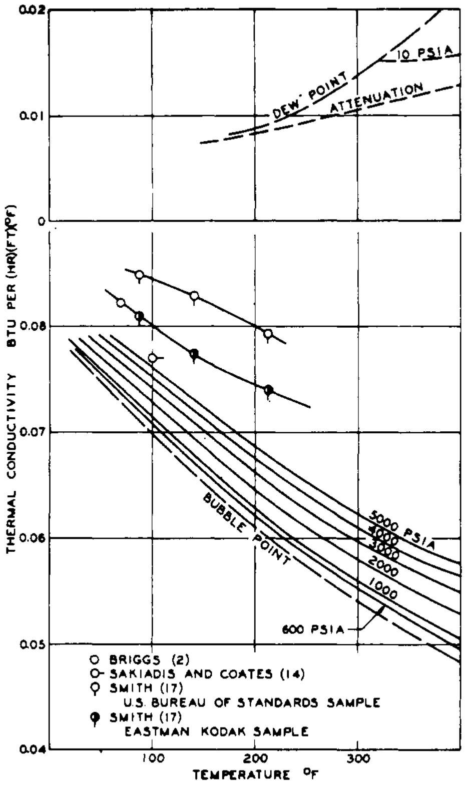

Figure 4. Effect of temperature upon the thermal conductivity of *n*-decane

for the thermal conductivity of *n*-decane in the gas phase are presented in Figure 3. All the measurements were made at pressures well below atmospheric to avoid proximity to dew point. Some difficulties were experienced in obtaining satisfactory reproducibility of the data shown in Figure 3. Such behavior may well have resulted from the presence of traces of impurities in the small quantity of *n*-decane gas present at relatively low pressures in the thermal conductivity cell. The authors believe that the over-all uncertainties in the measured thermal conductivity of *n*-decane in the gas phase were approximately three times those

Table II. Thermal Conductivity of *n*-Decane

Pressure, P.S.I.A.	Temperature, ° F.						
	40	100	160[a]	220	280[a]	340	400[b]
		(0.073)[c]	(0.40)	(1.59)	(5.08)	(13.49)	(31.19)
Bubble Point	0.0757	0.0697	0.0644	0.0596	0.0553	0.0516	0.0482
Attenuation	...	...	0.0076[d]	0.0087	0.0100	0.0114	0.0128
10	0.0757[e]	0.0697	0.0644	0.0596	0.0554	0.0151[f]	0.0158[f]
200	0.0759	0.0700	0.0647	0.0599	0.0557	0.0520	0.0486
400	0.0762	0.0704	0.0651	0.0603	0.0561	0.0525	0.0491
600	0.0764	0.0707	0.0654	0.0606	0.0565	0.0529	0.0495
800	0.0766	0.0710	0.0657	0.0610	0.0569	0.0533	0.0500
1000	0.0768	0.0714	0.0661	0.0613	0.0573	0.0537	0.0505
1500	0.0773	0.0721	0.0669	0.0621	0.0583	0.0548	0.0517
2000	0.0778	0.0728	0.0677	0.0630	0.0592	0.0559	0.0529
2500	0.0783	0.0735	0.0685	0.0638	0.0600	0.0568	0.0540
3000	0.0788	0.0741	0.0692	0.0646	0.0608	0.0576	0.0549
3500	0.0792	0.0747	0.0699	0.0654	0.0615	0.0583	0.0558
4000	0.0797	0.0751	0.0705	0.0661	0.0622	0.0590	0.0565
4500	0.0801	0.0755	0.0711	0.0667	0.0628	0.0596	0.0571
5000	0.0804	0.0759	0.0715	0.0673	0.0635	0.0602	0.0576
σ[g]	0.0001	0.0002	...	0.0001	...	0.0001	...

[a] Values for this temperature interpolated. [b] Values for this temperature extrapolated. [c] Two phase pressure of *n*-decane expressed in pounds per square inch, absolute. [d] Extrapolated. [e] Thermal conductivity expressed in B.t.u./(hr.)(ft.)(° F.). [f] Gas phase. [g] Standard error of estimate, σ, expressed in B.t.u./(hr.)(ft.)(° F.): $\sigma = [\sum_{1}^{N} (k_e - k_s)^2/(N-1)]^{1/2}$.

in the liquid phase. The standard deviation (*10*) of the data for each thermocouple from the values reported in Table I in the liquid phase is 0.0013 B.t.u. per (hour) (foot) (° F.), while it is 0.00022 in the gas phase. Probably, the over-all uncertainties of the measurements in the gas phase and liquid phase did not exceed 2%, although it was difficult to ascribe such a simple measurement of uncertainty as a whole.

The influence of temperature on the thermal conductivity of *n*-decane in the liquid phases is shown in the lower part of Figure 4. The other limited experimental investigations that have been made of the thermal conductivity of *n*-decane in the liquid phase at atmospheric pressure are also included in Figure 4. The early measurements of Smith (*17*) upon two samples of decane indicate some of the difficulties that were experienced in attempting to obtain pure *n*-decane three decades ago. Briggs (*2*) obtained a single value that is in good agreement with one of Smith's samples, and Sakiadis and Coates (*14*) reported a single value that is about 10% above the present data. All of the earlier data are well above the values obtained in the present study. As a result of the much more limited information in the gas phase, the data depicted in the upper part of Figure 4 have been shown by dashed lines only. Smooth values of thermal conductivity of *n*-decane in the gas and liquid regions are presented in Table II. These data are based upon graphical smoothing operations on large scale diagrams similar to the information presented in Figures 2, 3, and 4. Values reported in Table II for the bubble-point liquid were obtained by extrapolation to the indicated vapor pressure which was obtained from equilibrium measurements (*13*). In carrying out these extrapolations, no consideration was given to the singularities in the critical region reported by Sengers (*15*, *16*), Kramer and Comings (*8*), and Needham and Ziebland (*9*). Data at attenuation were obtained by extrapolation of the information presented in Figure 3 to low pressures and for the most part have been recorded to one less significant figure than for other states. The standard error of estimate of the smooth data from the experimental values is presented in Table II for each of the several temperatures. As the result of the limitation of the data in the gas phase and the small variation of specific volume in the liquid phase with change of state, no presentation of the effect of specific weight upon the residual thermal conductivity of *n*-decane has been indicated.

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NOMENCLATURE

d = differential operator
k = thermal conductivity, B.t.u./(hr.)(ft.)(° F.)
N = number of points
$q_m/d\theta$ = measured rate of energy addition, B.t.u./hr.
s = standard deviation defined in Table I
Δt_m = measured temperature difference, ° F.
θ = time, hr.
σ = standard error of estimate defined in Tables I and II
Σ = summation operator

Superscript

= uncorrected for effect of pressure

Subscripts

av = average
e = experimental
s = smoothed

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