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RECEIVED for review July 5, 1968. Accepted October 21, 1968. This paper was accepted as a contribution to this journal by R. L. Pigford, Editor of *Ind. Eng. Chem. Fundamentals.* Research supported in large part by Grant GP 2357 from the National Science Foundation.

Thermal Conductivity of Fluids

n-Pentane

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The thermal conductivity of *n*-pentane was measured at pressures up to 5000 p.s.i.a. in the temperature interval between 40° and 340° F. The data were obtained with a conductivity cell of spherical section. The results are presented in graphical and tabular form.

EXPERIMENTAL information concerning the thermal conductivity of *n*-pentane is limited almost entirely to measurements near atmospheric pressure for the gas phase (*5, 20, 21, 23*). A few measurements in the liquid phase are available at pressures near that of the atmosphere (*4, 40, 41*).

Some progress has been made in predicting the thermal conductivity of the lighter paraffin hydrocarbons at attenuation (*14, 21, 36, 42*). However, it has not been found feasible to predict behavior at pressures markedly in excess of atmospheric. As a result of the absence of experimental data at elevated pressures and the relative ineffectiveness of the application of statistical mechanics to the prediction of such quantities, experimental measurements of the thermal conductivity of *n*-pentane were made in the temperature interval between 40° and 340° F., at pressures between atmospheric and 5000 p.s.i.a., in both gas and liquid phases. No attempt was made to carry out measurements in the critical region, above the temperature range of the experimental equipment employed.

EQUIPMENT AND METHODS

A spherical conductivity cell was employed (*29–31*). In principle, the apparatus consisted of an inner sphere approximately 3.5 inches in diameter. Within it was located a specially constructed electric heater that yielded nearly uniform flux around the external surface of the sphere. The inner sphere was mounted within a spherical cavity that was part of the pressure vessel. The entire apparatus was submerged in an agitated liquid bath, whose temperature was controlled by a modulating electrical circuit so that it did not vary with respect to either time or position by more than 0.003° F. The radial transport path between the outer surface of the inner sphere and the inner surface of the spherical cavity was approximately 0.02 inch. Small thermocouples located near the outer surface of the inner sphere and the inner surface of the outer spherical shell permitted the temperature of both surfaces to be established. Corrections were applied for the location of the thermocouples within the stainless steel body of the sphere and the shell (*29*). Dimensions of the inner sphere and the outer shell were established by direct measurement. Appropriate corrections were made for the changes in the length of the radial transport path with changes in temperature and pressure. Such corrections did not amount to more than 1.0% in the resulting value of thermal conductivity.

At most states the measurements were carried out at four different values of thermal flux. Six active thermocouple pairs were employed in establishing the temperature differences, Δt_m, around the spherical transport path. The value of the quantity $[(q_m/d\theta)/\Delta t_m]$ was established for each thermocouple for each level of flux. Individual corrections for the location of the thermocouples below the surface of the sphere and of the shell were applied after the limiting value at zero flux of this derivative was obtained by application of linear regression analysis to all the points treated as a single group.

As a result of the change in average temperature of the phases and with the possibility of local convection at the higher fluxes, there was a significant variation in the apparent thermal conductivity $[(q_m/d\theta)/\Delta t_m]$ with thermal flux. The onset of gross convection could be established easily by the rapid rise in the apparent thermal conductivity with flux. In the investigation of *n*-pentane, no measurements were carried out where gross convection was encountered. In carrying out the regression analysis, it was assumed that the variation in the apparent thermal conductivity with respect to thermal flux was the same for each thermocouple.

To follow the over-all performance of the instrument, the thermal conductivity of helium was measured before, during, and after the measurements of *n*-pentane. The helium measurements were carried out near atmospheric pressure at 130° and 220° F. Variations in the behavior of the equipment during the investigation of *n*-pentane were not more than 0.2%. As had been experienced earlier (*6, 9, 12*), difficulty was encountered in removing all of the relatively high molecular weight paraffin hydrocarbons from the interstices of the equipment. Numerous prolonged evacuations and subsequent fillings with helium at atmospheric pressure were required to eliminate traces of *n*-pentane from the instrument. The adsorption of *n*-pentane on the surfaces of the seals used in the inner sphere and in the outer shell into the helium was the primary cause of the difficulties in obtaining a pure sample of helium. Since the thermal conductivities of the helium and the *n*-pentane were markedly different, small traces of *n*-pentane in the helium exerted a pronounced influence upon the apparent thermal conductivity of the helium. Table I shows the values of the measured thermal conductivity of helium as a function of time over the past decade. Corresponding values recommended by Hilsenrath and Touloukian (*15*) and other investigators (*17, 26, 43*) have been included for comparison.

The temperatures were measured by means of a strain-free platinum resistance thermometer which was compared recently with the indications of a similar instrument calibrated at the National Bureau of Standards. The temperature of the bath was known relative to the international platinum scale within 0.01° F. throughout the range of temperatures covered in this investigation.

The pressures were measured by a manometer at low pressures and by means of a balance utilizing a piston-cylinder combination (*27, 33*) for the higher pressures. This balance was connected directly to the thermal conductivity cell through an oil-filled, stainless steel, aneroid-type diaphragm (*35*). The piston-cylinder combination was calibrated against the vapor pressure of carbon dioxide at the ice point (*16, 18, 19*). The pressures were known within 0.2 p.s.i. or 0.1%, whichever is the larger measure of uncertainty.

MATERIALS

The helium employed in this investigation was reported by the vendor to contain less than 0.0003 mole fraction of impurities. The *n*-pentane was purchased from the Phillips Petroleum Co. as research grade material, with a reported purity of 0.9998 mole fraction *n*-pentane. The specific weight of the *n*-pentane sample was 38.767 pounds per cu. foot at 77° F., and the index of refraction of the sample relative to the *D*-lines of sodium was 1.3544 at 77° F., compared to 38.792 pounds per cu. foot and 1.35472 (*2*), respectively, reported for the same temperature as a critically chosen value for an air-saturated sample. Apparently, the purity of the material was as reported by the vendor and the impurities, for the most part, were probably isopentane (2-methylbutane) and unsaturated hydrocarbons containing five carbon atoms per molecule. The *n*-pentane was introduced into the equipment by conventional weighing-bomb techniques, after repeated evacuations followed by purging of the thermal conductivity equipment with *n*-pentane.

For studies in the gas phase the equipment was filled to the desired pressure from a small weighing bomb (*33*). The equipment was cooled to approximately 30° F. and filled with *n*-pentane for measurements in the liquid phase. An increase in temperature caused a rapid rise in pressure, to permit measurements at 5000 p.s.i.a. for a temperature of 40° F. At the higher temperatures *n*-pentane was withdrawn from the thermal conductivity equipment to adjust the pressure to the desired value.

EXPERIMENTAL RESULTS

The effect of thermal flux upon the apparent thermal conductivity $[(q_m/d\theta)/\Delta t_m]$ for each of the six thermocouples is presented in Figure 1. After the influence of the position of the thermocouples had been taken into account, the apparent thermal conductivity was calculated for each of

Table I. Thermal Conductivity of Helium from Several Sources

			Thermal Conductivity, B.T.U./(Hr.)/(Ft.)(° F.)				
Date	Pressure, P.S.I.A.	Temp., ° F.	Authors	Keyes[a]	Hilsenrath, Touloukian[b]	Wilson[a]	Powell, Ho, Liley[a]
			Atmospheric Pressure				
1961	16.3	40	0.08204	0.08273	0.08257		0.08165
1959	15.0	100	0.08853	0.08864	0.08854	0.0890	0.08750
1960	18.9	100	0.08854				
1961	16.6	100	0.08859				
1964	18.1	100	0.08824				
1962[c]	17.7	130	0.09169	0.09150	0.09135		0.09064
1963[c]	16.4	130	0.09130				
1964[c]	17.3	130	0.09094				
1966[c]	17.1	130	0.09108				
1968	17.3	130	0.09179				
	17.4	130	0.09143				
1959	17.7	220	0.09947	0.09960	0.09941		0.09878
1960	18.1	220	0.09946				
1968	17.6	220	0.09989				
1959[c]	15.0	340	0.10954	0.10957	0.10936		0.11003
1960[c]	18.4	340	0.10927				
Av. deviation[d]				0.00025	0.00018	0.00052	0.00070

[a] Statistical mechanical calculations and experimental data (*17, 25, 41*). [b] Critical review (*15*). [c] Average value for given year. [d] Average deviation expressed as:

$$s' = \sum_{1}^{N_p} \frac{|(k_e)_{\text{av}} - k_r|}{N_p}$$

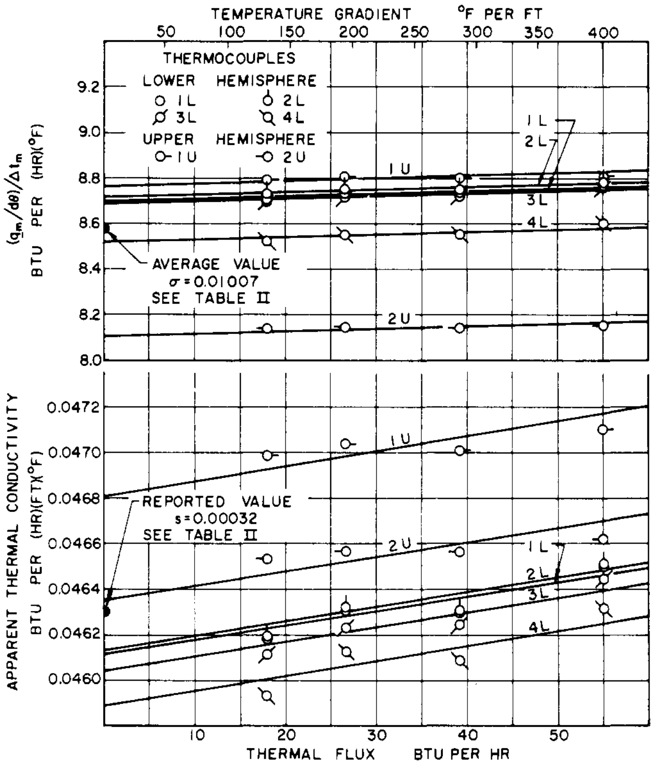

Figure 1. Effect of thermal flux upon apparent thermal conductivity at 280° F. and 1087 p.s.i.a.

the experimental points. The result is shown as a function of thermal flux in the lower part of the figure. The values at zero thermal flux were averaged to obtain the reported value of apparent thermal conductivity. The standard error of estimate of experimental points from the curves drawn in Figure 1 was 0.01007 B.t.u./(hr.)(° F.). The information presented in Figure 1 was for a pressure of 1087 p.s.i.a. and a temperature of 280° F. The temperature gradient in the radial transport path has been indicated in the upper part of the figure.

The uncertainties in each of the primary measurements, in the associated standard deviations between the thermocouples, and in the standard error of estimate of the experimental points from the smooth curves, are presented in Table II. The absolute uncertainty in a single measurement of thermal conductivity can be estimated from a review of this information, to arrive at the uncertainty in the over-all group of data, which, in the final analysis, is a matter of judgment.

The behavior indicated in Figure 1 is typical of the results obtained. At the higher pressures there was a slight deformation of the outer shell and the inner sphere, which resulted in a small lack of concentricity and increased somewhat the differences in the behavior found in the lower and upper hemisphere. A review of the behavior of the instrument (*6*) demonstrates that the use of a spatial average of the indications of the apparent thermal conductivity at zero flux is a satisfactory means of obtaining the proper values to employ for a given state. The lack of concentricity at the higher pressures did not introduce more than 0.2% uncertainty in the results. The change in length of the transport path upon change in pressure and temperature was taken into account, utilizing the known properties of the stainless steel involved.

The experimental values of the thermal conductivity of *n*-pentane after extrapolation to zero thermal flux are presented in Table II. In addition, information concerning each state, such as the number of flux values, the maximum flux, and the number of experimental points obtained, are tabulated. To make the standard error of estimate more meaningful to the reader, the average value of the quantity $[(q_m/d\theta)/\Delta t_m]$ for the limiting value of zero thermal flux has been included. The standard error of estimate recorded corresponds to the deviation of experimental points from the straight lines shown in Figure 1 for each of the several experimental points. The standard deviation of the six thermocouples when extrapolated to zero thermal flux for the above-mentioned average value is included. The gradient listed in Table II is the average value of the slope of the straight lines as shown in Figure 1. As expected, there is some variation in the gradient with state.

The thermal conductivities of the gas phase taken from Table II are shown in Figure 2. The standard error of estimate of these experimental data from the smooth curves drawn through them is 0.00007 B.t.u./(hr.)(ft.)(° F.). The curves have been extended to the vapor pressure of *n*-pentane (*32*) and thus yielded values of the thermal conductivity for the saturated or dew point gas. The dashed curve for 400° F. was extrapolated from the data at the lower temperature. Figure 3 depicts the behavior in the liquid phase. As a matter of interest, the smooth curves shown in Figure 2 have been included to give an over-all portrayal of the effect of state upon the thermal conductivity of *n*-pentane within the range of pressures and temperatures covered in this investigation. The standard error of estimate of the experimental points from the smooth curves shown is 0.00018 B.t.u./(hr.)(ft.)(° F.). Values extrapolated to 400° F. have been included at the higher and lower pressures. However, behavior in the critical region was not investigated, and no attempt was made to predict behavior in this region. No effort has been made to extend the behavior predicted for dew point and bubble point to temperatures above 340° F.

The effect of temperature upon the thermal conductivity of *n*-pentane is shown in Figure 4. Again, behavior in the critical region for temperatures above 340° F. was not included. Rather anomalous behavior involving unusually large values of thermal conductivity in the critical region exists, according to recent reviews from Michels (*22*) and Sengers (*37-39*).

Smooth values of the thermal conductivity of the *n*-pentane are reported in Table III. The vapor pressure was established from available experimental data (*32*). As indicated earlier, the behavior at dew point and at bubble point was established by extrapolation of the data from lower and higher pressures, respectively, to the vapor pressure. From a critical assessment of the uncertainties of each of the primary variables and the stability of the over-all performance of the equipment, it is probable that the values recorded in Table III do not involve uncertainties of more than 0.4%.

Residual thermal conductivity as used in this investigation represents the difference between the thermal conductivity at attenuation and that at the state in question for the same temperature. Attenuation is designated as that state at which the fluid can be considered as continuous in nature, and yet the deviation from zero pressure is sufficiently small that simple assumptions may be used to predict the thermal conductivity of many molecules from statistical-mechanical considerations (*13, 14*). Residual thermal conductivity is often known as a "thermal conductivity excess." It was predicted by Abas-Zade (*1*) that the residual thermal conductivity would be a single-valued function of specific weight. This behavior has been confirmed by several investigators (*25, 34*). More recently, however, Michels (*22*) and Sengers (*37-39*) reviewed a relatively large body of thermal conductivity data and presented evidence that the residual thermal conductivity is not a single-valued function of specific weight in the critical region. This point of view is confirmed by the recent work of Bailey and Kellner (*3*) and Needham and Ziebland (*24*). These matters

Table II. Experimental Conditions

Pressure, P.S.I.A.	No. of Flux Values	Maximum Flux, B.t.u./(Hr.)	No. of Points	Gradient[a], ° F.$^{-1}$	Average[b] $(q_m/d\theta)/\Delta t_m$, B.t.u./(Hr.)(° F.) $q_m = 0$	Standard Error of Estimate[c], B.t.u./(Hr.)(° F.)	Thermal Conductivity B.t.u./(Hr.)(Ft.)(° F.)	Standard Deviation[d], B.t.u./(Hr.)(Ft.)(° F.)
40° F.								
3.6	4	18.83	24	0.00053	1.57203	0.00409	0.007929	0.000089
164	4	61.81	24	−0.00192	11.58632	0.02142	0.067359	0.000332
1001	4	62.78	24	−0.00007	11.70727	0.02787	0.068602	0.000300
2981	4	62.32	24	−0.00050	12.05100	0.01421	0.072153	0.001474
4957	4	58.34	24	−0.00103	12.29998	0.01364	0.075138	0.002800
100° F.								
12.5	4	19.33	24	0.00392	1.81750	0.00213	0.009149	0.000074
172	4	59.03	24	−0.00008	10.51637	0.01418	0.059291	0.000344
1103	4	59.96	24	0.00045	10.79072	0.00962	0.061449	0.000188
2958	4	61.79	16	0.00100	11.02523	0.01204	0.064986	0.000991
4685	4	62.51	16	0.00292[e] 0.00128[f]	11.26290	0.03239	0.067689	0.001912
160° F.								
26	4	19.80	24	0.00254	2.21678	0.00481	0.011205	0.000113
220° F.								
17	4	20.86	24	0.00398	2.58527	0.00222	0.013042	0.000063
25	4	21.79	24	0.00331	2.60100	0.00148	0.013125	0.000061
49	4	22.13	24	0.00397	2.60728	0.00237	0.013164	0.000078
73	4	23.59	24	0.00321	2.64143	0.00546	0.013337	0.000058
264	4	62.65	24	0.00107[e] −0.00034[f]	8.84282	0.00778	0.048084	0.000379
1091	4	58.87	24	0.00184[e] −0.00086[f]	9.18615	0.02031	0.050487	0.000774
2806	4	61.19	16	0.00017	9.80495	0.01529	0.055473	0.001013
3055[g]	4	62.52	24	0.00125[e] −0.00044[f]	9.83205	0.00752	0.055098	0.001274
4816	4	62.27	16	0.00005	12.76803	0.00947	0.059382	0.001998
280° F.								
17	4	24.65	24	0.00366	3.02795	0.00309	0.015287	0.000063
100	4	24.33	24	0.00350	3.08642	0.00271	0.015600	0.000072
175	4	27.75	24	0.00408	3.19553	0.01414	0.016186	0.000097
363	4	50.43	24	0.00121	8.12843	0.01167	0.043434	0.000157
1087	4	54.98	24	0.00112	8.58243	0.01007	0.046301	0.000317
2980	4	56.37	24	0.00169	9.27127	0.01223	0.051092	0.001021
4981	4	61.66	24	0.00090	9.83525	0.01718	0.055317	0.001829
340° F.								
17	4	29.38	24	0.00390	3.48188	0.00575	0.017582	0.000049
100	4	31.02	24	0.00405	3.53508	0.00704	0.017870	0.000057
200	4	30.29	24	0.00343	3.67012	0.00250	0.018594	0.000070
300	4	29.65	24	0.00223	3.97848	0.00585	0.020246	0.000077
514	4	50.35	24	0.00543[e] 0.01607[f]	7.46918	0.09050	0.039186	0.000578
1082	4	51.10	24	0.00313[e] 0.00130[f]	7.98303	0.00693	0.042548	0.000378
2940	4	49.64	24	0.00134	8.89035	0.00878	0.048350	0.000784
5110	4	50.17	24	0.00213	9.47505	0.01727	0.052627	0.001575

[a] Average value of $d\,[(q_m/d\theta)/\Delta t_m]/d(q_m/d\theta)$ for all thermocouple measurements, which correspond to average slope of straight lines shown in Figure 1. [b] Numerical average, not area-weighted average. [c] Standard error of estimate of $[(q_m/d\theta)/\Delta t_m]_e$ from linear regression analysis of data from each of several thermocouples:

$$\sigma = \left[\left\{\sum_{1}^{N_p}\left[\left(\frac{q_m/d\theta}{\Delta t_m}\right)_e - \left(\frac{q_m/d\theta}{\Delta t_m}\right)_s\right]^2\right\}/(N_p - 1)\right]^{1/2}$$

[d] Standard deviation from area-weighted average of indication of six thermocouples at zero flux:

$$s = \left[\sum_{1}^{N_p}(k'_{\text{av}} - k')^2/N_p\right]^{1/2}$$

[e] Average value of gradient of thermocouples in lower hemisphere. [f] Average value of gradient of thermocouples in upper hemisphere. [g] Check measurement.

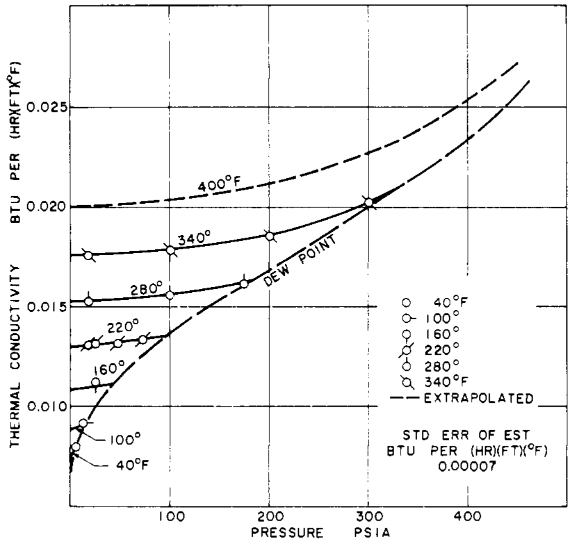

Figure 2. Thermal conductivity of *n*-pentane in the gas phase

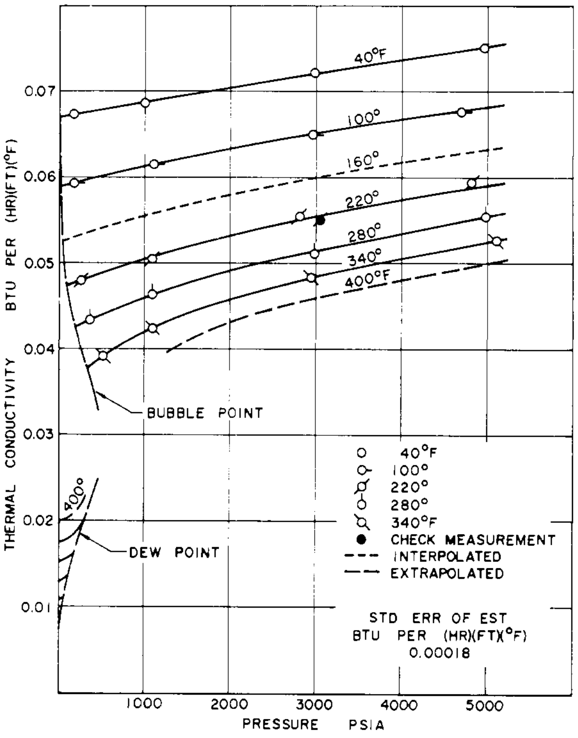

Figure 3. Thermal conductivity of *n*-pentane in the liquid phase

are discussed in some detail by Reid and Sherwood (*28*). On the other hand, the viscosity excess for the paraffin hydrocarbons (*7, 8, 10, 11*) appears to be a single-valued function of specific weight.

The residual thermal conductivity of *n*-pentane is shown in Figure 5. The data at specific weights near that of the critical state are in doubt, since no experimental information was available to establish behavior in this region. The behavior at low pressures corresponding to the gas phase is shown on an enlarged scale in the upper part of the diagram. The following analytical expression was fitted by linear regression analysis to the experimental data shown in Figure 5.

$$k - k_o = a\sigma + b\sigma^2 + c\sigma^3 + d\sigma^4 \qquad (1)$$

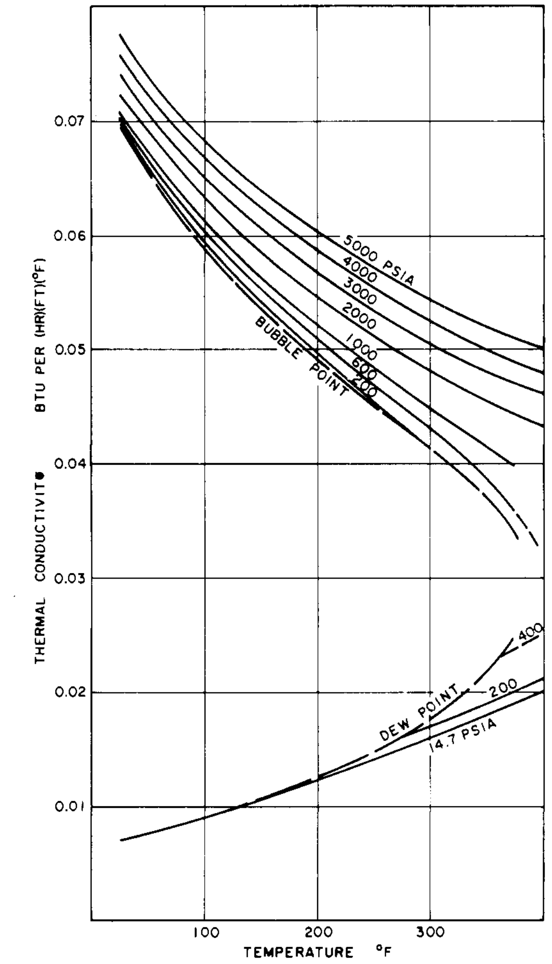

Figure 4. Influence of temperature upon thermal conductivity of *n*-pentane

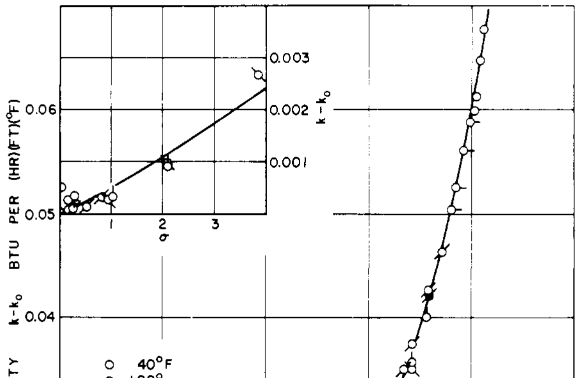

Figure 5. Residual thermal conductivity of *n*-pentane

Table III. Thermal Conductivity of *n*-Pentane

Pressure, P.S.I.A.	Temperature, ° F.						
	40	100	160	220	280	340	400[a]
	(4.30)[b]	(15.7)	(42.5)	(94.9)	(185.6)	(329.2)	
Dew point	0.00794	0.00917	0.01108	0.01348	0.01630	0.02103	
Bubble point	0.06707	0.05887	0.05260	0.04742	0.04267	0.03782	
Attenuation	0.00740[c]	0.00890	0.01083	0.01300	0.01525	0.01757	0.02002
14.7	0.06709[d]	0.00915	0.01088	0.01303	0.01528	0.01758	0.02003
200	0.06739	0.05932	0.05311[e]	0.04780	0.04273	0.01859	0.02118
400	0.06770	0.05982	0.05373	0.04852	0.04359	0.03836	0.02525
600	0.06802	0.06030	0.05434	0.04921	0.04442	0.03974	0.03147
800	0.06834	0.06076	0.05491	0.04990	0.04522	0.04100	0.03550
1000	0.06869	0.06120	0.05548	0.05050	0.04600	0.04212	0.03780
1500	0.06952	0.06223	0.05671	0.05198	0.04770	0.04423	0.04112
2000	0.07038	0.06321	0.05781	0.05318	0.04917	0.04582	0.04310
2500	0.07123	0.06417	0.05885	0.05433	0.05031	0.04723	0.04467
3000	0.07204	0.06508	0.05983	0.05536	0.05142	0.04848	0.04595
3500	0.07282	0.06594	0.06075	0.05630	0.05253	0.04949	0.04699
4000	0.07360	0.06672	0.06163	0.05723	0.05349	0.05042	0.04792
4500	0.07441	0.06742	0.06241	0.05820	0.05444	0.05140	0.04892
5000	0.07521	0.06812	0.06315	0.05901	0.05539	0.05240	0.04987
σ[f]	0.00009	0.00001	...	0.00034	0.00012	0.00002	...

[a] Values for this temperature extrapolated. [b] Vapor pressure of *n*-pentane expressed in p.s.i.a. [c] Extrapolated. [d] Thermal conductivity expressed in B.t.u./(hr.)(ft.)(° F.). [e] Values at this temperature and higher pressures interpolated. [f] Standard error of estimate, σ, expressed in B.t.u./(hr.)(ft.)(° F.).

$$\sigma = \left[\sum_{1}^{N_p} (k_e - k_s)^2 / (N_p - 1) \right]^{1/2}$$

The standard error of estimate of all the experimental data shown in the figure from this analytical expression was 0.00040 B.t.u./(hr.)(ft.)(° F.). The smooth curve shown in Figure 5 is a representation of Equation 1. This equation gives a continuous set of values for the thermal conductivity excess, even in the critical region. The authors are of the opinion that such behavior probably does not exist in this region, and that care must be exercised in utilizing Equation 1.

Figure 6 presents the influence of temperature upon thermal conductivity of *n*-pentane at attenuation. The current measurements are slightly higher than the measurements of Bromley (*5*), Mann (*21*), and Missenard (*23*), but agree very well with the measurements of Lambert (*20*). The following analytical expression has been fitted to the current experimental data of Figure 6 by linear regression analysis.

$$k_o = A + BT + CT^2 + DT^3 \qquad (2)$$

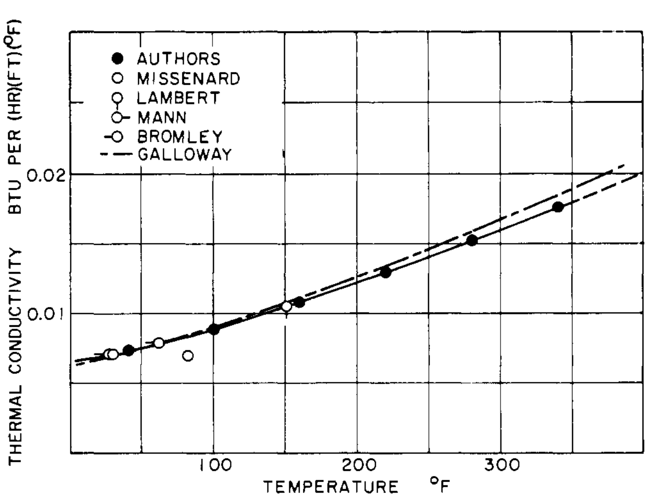

Figure 6. Thermal conductivity of *n*-pentane at attenuation

The deviation of the points from the analytical expression was an order of magnitude smaller than the experimental uncertainty. The standard error of estimate of all the points from Equation 2 shown in Figure 6 was 0.00046 B.t.u./(hr.)(ft.)(° F.). A simple combination of Equations 1 and 2 yields the following expression for the thermal conductivity of *n*-pentane in terms of the specific weight and temperature of the phase.

$$k = [A + BT + CT^2 + DT^3] + [a\sigma + b\sigma^2 + c\sigma^3 + d\sigma^4] \qquad (3)$$

This expression may not be applicable in the critical region.

ACKNOWLEDGMENT

H. H. Reamer contributed to the experimental program and Virginia Berry to the linear regression analysis of the experimental results.

NOMENCLATURE

A, B, C, D = coefficients, B.t.u./(hr.)(ft.)(° F.)
a, b, c, d = coefficients, B.t.u./(hr.)(ft.)(° F.)
d = differential operator
k = thermal conductivity, B.t.u./(hr.)(ft.)(° F.)
k_o = thermal conductivity at attenuation, B.t.u./(hr.)(ft.)(° F.)
k' = thermal conductivity uncorrected for effect of pressure on instrument, B.t.u./(hr.)(ft.)(° F.)
N_p = number of points
$q_m/d\theta$ = measured rate of energy addition, B.t.u./hr.
s = standard deviation defined in Table II
s' = average deviation defined in Table I
Δt_m = measured temperature difference, ° F.
θ = time, hr.
σ = specific weight, lb./cu. ft.
σ = standard error of estimate defined in Tables II and III
$\sum$ = summation operator

Subscripts

av = average
e = experimental
o = attenuation
r = reference
s = smooth

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RECEIVED for review August 5, 1968. Accepted October 21, 1968. This paper was accepted as a contribution to this journal by R. L. Pigford, Editor of *Ind. Eng. Chem. Fundamentals*. A substantial part of the experimental work carried out with the support of a National Science Foundation Grant, GK-715.