Viscosity of Hydrocarbons

n-Decane

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The viscosity of *n*-decane was measured at temperatures between 220° and 400° F. in the gas phase at pressures well below the vapor pressure. The viscosity of *n*-decane in the liquid phase was measured at pressures as high as 5000 p.s.i. in the temperature interval between 40° and 400° F. Good agreement with other investigators was obtained for the liquid phase, and reasonable agreement with the prediction of the viscosity of *n*-decane gas at attenuation by statistical mechanical considerations. The data are presented in graphical and tabular form.

THE viscosity of *n*-decane in the liquid phase at pressures near that of the atmosphere has been investigated in some detail. This experimental work has been reviewed critically and summarized (*1*). No further reference to such numerous investigations in the past several decades at pressures near that of the atmosphere is made here. Measurements in the liquid phase of *n*-decane were made at elevated pressures by Lee and coworkers (*10*) at temperatures between 100° and 340° F. for pressures up to 8000 p.s.i.a., in a viscometer involving flow of the liquid through a capillary tube. Apparently no experimental measurements have been made heretofore upon the viscosity of *n*-decane in the gas phase.

To confirm the measurements of Lee (*10*) at elevated pressures for *n*-decane in the liquid phase with a markedly different type of instrument and to establish some information concerning the viscosity of *n*-decane in the gas phase, a series of measurements was made at temperatures between 40° and 400° F. for pressures up to 5000 p.s.i.a., in a rotating-cylinder viscometer which has been described in some detail (*12*). In principle, the viscometer consists of a rotating cylinder within which a stator is suspended on a platinum-tungsten wire. The angular deformation resulting from the viscous drag on this cylinder was measured. Sufficient information concerning the torsional elastic constant of the suspension and the dimensions of the instrument as a function of pressure and temperature are known that it may be used as an absolute device. The standard deviation of the measured viscosity of helium at atmospheric pressure and 100° F. from accepted values (*9*) was 1.3% over a 2-year period.

The dimensions of the instrument were sufficiently stable during the period of this investigation to make it improbable that the width of the annular gap surrounding the stator varied by more than 0.1%. The elastic constants of the suspension were determined directly (*12, 14*) and are believed to be known within 0.2%. The angular deformation could be established with an uncertainty of not more than 0.2%. Measurements were made with the rotating sleeve operating in both directions. The results were averaged, and the deviation of the individual measurements from the average was 0.2%.

Temperature was determined by means of a strain-free, platinum resistance thermometer, calibrated against a similar instrument whose behavior had been determined by the National Bureau of Standards. It is believed that the temperatures were established within 0.05° F. relative to the international practical temperature scale of 1948 throughout the interval between 40° and 400° F. Pressures were measured by means of a balance involving a piston-cylinder combination (*16*). Experience with this instrument (*16*) indicates that the pressures were known relative to the vapor pressure of carbon dioxide (*2*) at the ice point within 0.1 p.s.i. or 0.1%, whichever was the larger measure of uncertainty. The agreement of the experimental values of viscosity of helium at atmospheric pressure for a temperature of 100° F. with selected values (*9*) is set forth in Table I.

MATERIALS

The *n*-decane employed throughout this investigation was obtained as research grade from the Phillips Petroleum Co. Such a grade was reported to contain not more than 0.0051 mole fraction of materials other than *n*-decane. An air-free sample of the liquid yielded an index of refraction of 1.4095 relative to the *D*-line of sodium at 77° F., compared with a critically chosen value of 1.40967 (*1*) for an air-saturated sample of *n*-decane. The specific weight of the sample employed in this investigation at 77° F. and at atmospheric pressure was 45.3382 pounds per cu. foot compared to 45.337 pounds per cu. foot reported as a critically chosen value (*1*) for an air-saturated sample at the same temperature and pressure. It is believed that the above-indicated agreement of the index of refraction and of the specific weight give credence to the reported purities of such a grade of *n*-decane submitted by the vendor. The sample was used without further purification, except for refluxing at reduced pressures to remove dissolved air.

Table I. Viscosity of Helium at 100° F. and Atmospheric Pressure

Date	Pressure, P.S.I.A.	Viscosity, Micropoises	
		Authors	Hilsenrath (*9*)
October 1966	18.1	202.7[a]	203.1[b]
April 1967	17.7	199.7	
May 1967	17.7	200.0	
June 1967	17.2	201.4	
July 1967	17.2	201.3	
	σ[c]	3.69	
	s[d]	0.0127	

[a] Values tabulated are averages of a minimum of 3 measurements. [b] Value at 14.7 p.s.i.a. [c] Standard deviation expressed in micropoises and defined by

$$\sigma = \left[\sum_{1}^{N} (\eta_e - \eta_r)^2 / N \right]^{1/2}$$

[d] Average deviation expressed as fraction and defined by

$$s = \sum_{1}^{N} (\eta_e - \eta_r) / \eta e| / N$$

EXPERIMENTAL METHODS

In connection with studies of the viscosity in the liquid phase, conventional high vacuum techniques were employed in the introduction of the *n*-decane, and the pressure was varied by the introduction and withdrawal of mercury from an associated pressure vessel as described (*5, 12*).

In the case of studies in the gas phase, unusual precautions were found necessary to ensure the elimination of traces of other compounds which could contaminate the sample. A number of measurements were carried out at pressures near 1 p.s.i.a. Small quantities of contaminants adsorbed on the walls of the viscometer could result in a significant change in composition of the gas phase and a measurable change in viscosity. To avoid such difficulties the equipment was evacuated for extended periods and refilled with *n*-decane for as many as five consecutive cycles. At the higher temperatures, which were encountered near the end of the investigation, some difficulty with measurements in the gas phase was experienced from the physical contamination of the rotating-cylinder viscometer with mercury. The mercury was transported through the low pressure gas phase interconnecting the pressure vessel; this eventually resulted in the presence of liquid mercury on the platinum-tungsten suspension employed. It became necessary to replace the suspension toward the end of the program.

EXPERIMENTAL RESULTS

The experimental measurements of the viscosity of *n*-decane in the gas and liquid phases are set forth in Table II. Each measurement results from at least two separate measurements of the angular deflection in each direction. The results have been tabulated to at least one more significant figure than is believed justified by the accuracy, in contradistinction to the precision, of the measurements. The effect of pressure upon the viscosity of the liquid phase is shown in Figure 1. The standard error of estimate of the experimental data from the smooth curves was 56.3 micropoises. It is apparent that the effect of pressure and temperature upon the viscosity of *n*-decane is similar in general nature to the behavior found for other hydrocarbons (*3–6, 12*).

The viscosity of *n*-decane in the liquid phase at atmospheric pressure is compared with the data of other investigators in Figure 2. The critically chosen values for atmospheric pressure (*1*) have been presented here. The values extrapolated from the measurements by Lee (*10*) and the critically chosen values (*1*) are in good agreement with the current investigation. It appears that the maximum deviation at atmospheric pressure among the three sets of data was 130 micropoises, and the standard error of estimate of the points shown in Figure 2 from the smooth curve was 119.9 micropoises.

Table II. Experimental Measurements[a] for *n*-Decane

Pressure, P.S.I.A.	Viscosity, Micropoises	Pressure, P.S.I.A.	Viscosity, Micropoises
40° F.		220° F.	
16.3	12,244	1	64.4
16.9	12,222	1	65.8
100.7	12,151	16.5	3583
104.8	12,238	198.8	3612
1989.4	14,277	1995.7	4279
2013.2	14,227	3999.2	4905
3993.6	16,485	5052.8	5213
4022.4	16,599		
5085.4	17,856	280° F.	
5097.0	18,028		
		1	74.5
100° F.			
		340° F.	
16	7,271		
16	7,202	10	77.1
96.7	7,350	25.0	2113
1014.9	7,887	1028.6	2363
1047.2	7,739	2022.8	2619
1055.8	7,916	3111.2	2839
1084.8	7,900	4086.3	3041
2037.5	8,508	5063.0	3261
2089.6	8,542		
3045.4	9,040		
3060.0	9,100	400° F.	
3078.0	9,128		
3910.2	9,650	2	84.6
3931.3	9,685	16.0	84.2
3974.5	9,716	58.0	1601
5178.6	10,509	1011.3	1832
5201.5	10,601	3060.8	2247
5226.8	10,548	4999.7	2628

[a] Values tabulated represent average of a minimum of two measurements.

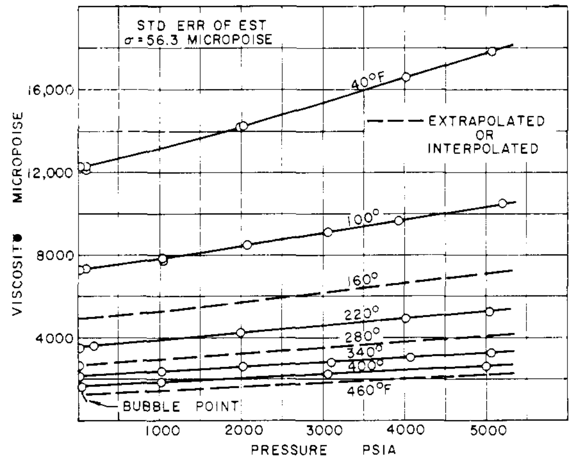

Figure 1. Viscosity of *n*-decane in the liquid phase

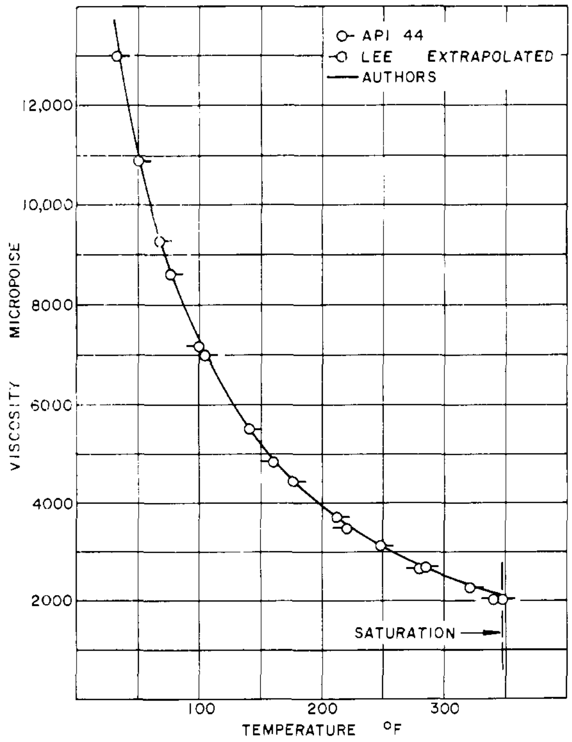

Figure 2. Comparison of viscosity from several investigations at atmospheric pressure

Figure 3 compares the measurements of Lee and coworkers (*10*) at elevated pressure with the authors' experimental information. The standard error of estimate of these measurements from the current data shown by a full line in Figure 3 is 99 micropoises. At the lower temperatures, Lee (*10*) shows a greater rate of change in viscosity with pressure than was found by the authors. Such satisfactory agreement between measurements made with widely different types of instruments is gratifying. It lends credence to the accuracy of the actual values of viscosity reported.

Figure 4 depicts an estimate of the effect of pressure upon the viscosity of *n*-decane in the gas phase for pressures substantially below vapor pressure. No regard was taken in the preparation of Figure 4 of the data recorded in Table II in estimating the effects of pressure upon the viscosity of *n*-decane in the gas phase. The influence of pressure was established by application of the quasi-theoretical corrections recommended by Galloway (*7, 8*) to the data. However, within the constraints of such corrections (*7, 8*) the data of Table II were employed to establish the lines shown in Figure 4. The accuracy of measurements in the gas phase is markedly lower than in the liquid phase. A portion of this difficulty may result in connection with the measurements at pressures of approximately 1 p.s.i.a., where traces of impurities were not completely eliminated by the experimental procedures outlined earlier.

The effect of temperature upon the viscosity of *n*-decane at attenution is shown in the lower part of Figure 4. In connection with the discussion of the gas phase data, the predicted viscosity of the gas phase of *n*-decane at attenuation (*8*) has been included for comparison with the experimental values. In this instance, the predicted values are somewhat lower than the experimental information. The difference amounts to approximately 3 micropoises throughout the entire temperature interval, or approximately 5% for a temperature of 220° F.

In Table III are recorded the smooth values of the viscosity of *n*-decane based upon the measurements reported in Table II. The standard error of estimate of the

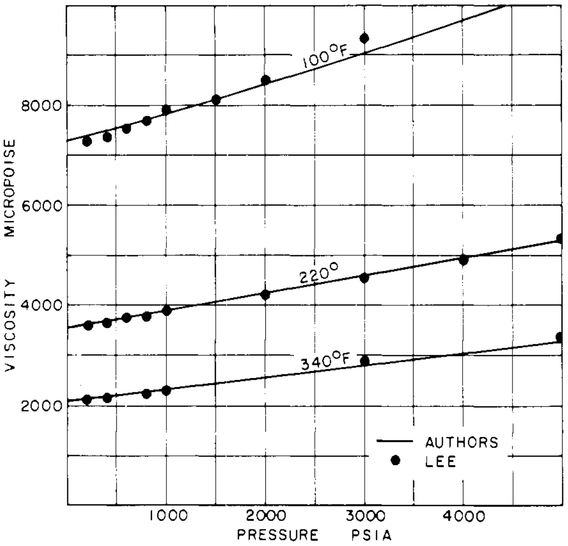

Figure 3. Comparison of effect of pressure upon viscosity of *n*-decane

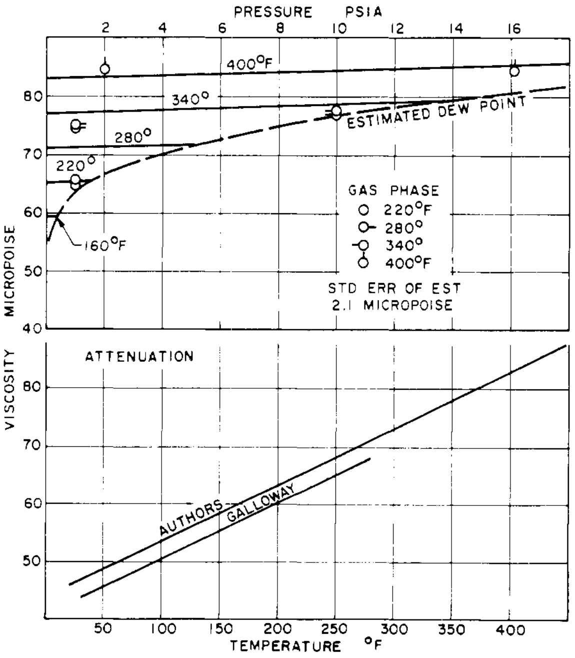

Figure 4. Viscosity of *n*-decane in gas phase

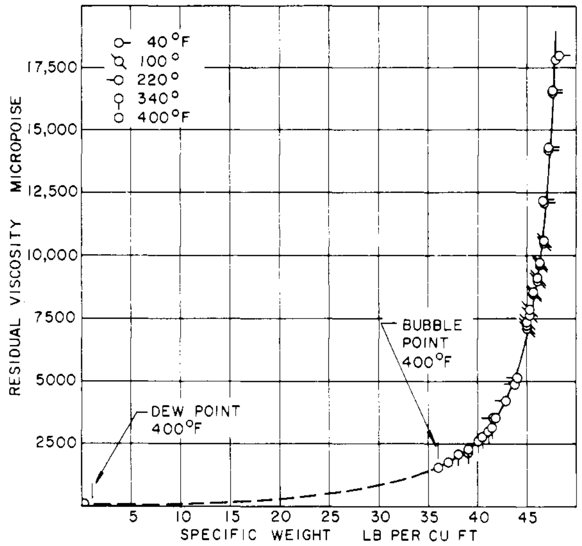

Figure 5. Residual viscosity of *n*-decane

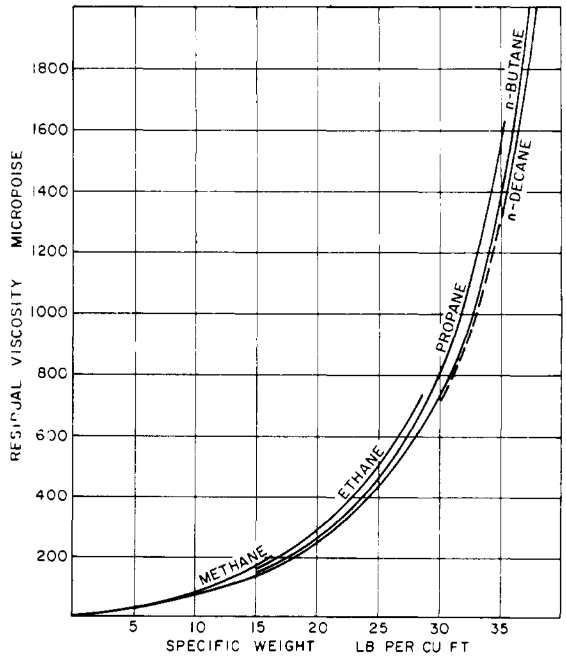

Figure 6. Residual viscosity for several hydrocarbons

Table III. Viscosity of *n*-Decane

Pressure, P.S.I.A.	Temperature, ° F. 40	100	160[a]	220	280[a]	340	400	460[b]
	(0.004)[c]	(0.073)	(0.40)	(1.59)	(5.08)	(13.49)	(31.19)	(64.72)
Dew point	47.8[d]	53.6	59.4	65.6	71.7	78.9	85.5	...
Bubble point	12250	7300	4910	3550	2710	2090	1600	1200
Attenuation	47.8[e]	53.6	59.4	65.3	71.0	76.9	82.7	...
14.7	12260	7310	4920	3560	2710	2100	85.4	...
200	12430	7410	5000	3630	2760	2150	1630	1220
400	12620	7510	5080	3700	2830	2200	1680	1270
600	12810	7630	5160	3760	2880	2250	1730	1310
800	13010	7740	5250	3830	2940	2290	1780	1360
1000	13200	7860	5340	3900	2990	2340	1820	1400
1500	13700	8140	5540	4080	3130	2460	1920	1510
2000	14230	8430	5760	4260	3270	2580	2020	1610
2500	14780	8740	5980	4420	3400	2700	2120	1710
3000	15350	9060	6190	4580	3540	2810	2220	1810
3500	15940	9380	6420	4740	3680	2910	2320	1910
4000	16550	9710	6640	4920	3810	3020	2430	2000
4500	17140	10040	6850	5080	3910	3140	2530	2100
5000	17760	10380	7070	5260	4080	3250	2630	2190
[f]	92.1	57.7		22.0		21.0	7.1	

[a] Values at this temperature interpolated from experimental data at lower and higher temperatures. [b] Values at this temperature extrapolated from experimental data at lower temperatures. [c] Values in parentheses represent vapor pressures expressed in p.s.i.a. [d] Viscosity at dew point estimated. [e] Viscosity expressed in micropoise. [f] Standard error of estimate for the liquid phase expressed in micropoises and defined by

$$\sigma = \left[\sum_{1}^{N} (\eta_e - \eta_s)^2 / (N-1) \right]^{1/2}$$

experimental data in Table II has been reported for each temperature. Values of the viscosity of *n*-decane at attenuation, together with the estimated values of the effect of pressure upon viscosity of the gas phase have been included. The results pertaining to the gas phase have been reported to one less significant figure than those of the liquid in order to emphasize the lower accuracy of the measurements in the gas phase.

The residual viscosity, defined as the difference between the viscosity of attenuation at a given temperature and the viscosity at the state in question, has been found (*3–6, 10*) to be a single-valued, nontemperature-dependent function of the specific weight. The residual viscosity for *n*-decane is shown in Figure 5. The specific weight of *n*-decane in the liquid phase was based on available volumetric information (*13*). In the gas phase it was established by the methods proposed by Pitzer (*11, 15*).

As a matter of interest, the residual viscosities of methane, ethane, propane, *n*-butane, and *n*-decane are shown in Figure 6. There appears to be a rather systematic variation in the residual viscosity with molecular weight.

The viscosities of methane, ethane, propane, *n*-butane, and *n*-decane at attenuation are shown in Figure 7. These data are all based on experiment and do not involve any of the semitheoretical considerations presented by Galloway (*8*). There is a progressive decrease in the viscosity at attenuation with an increase in molecular weight (*8*). As stated earlier, the data for *n*-decane in the gas phase involve more uncertainty than the data for the other hydrocarbons. The greater uncertainty may well result from the fact that most of the measurements were carried out at such a low pressure that traces of contaminants adsorbed on the interior surface of the apparatus may have caused sufficient change in composition to result in a measurable change in the viscosity of the gas phase.

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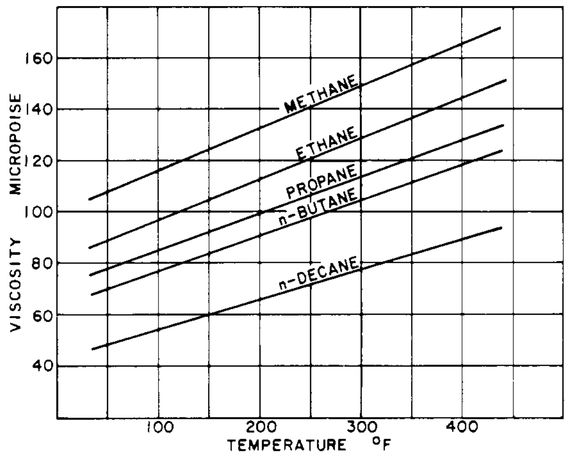

Figure 7. Viscosity of several hydrocarbons at attenuation

NOMENCLATURE

N = number of data points
s = average deviation, fraction (defined in Tables I and III)
η = viscosity, micropoises
Σ = summation operator
ς = specific weight, lb./cu. ft.
σ = standard deviation or standard error of estimate (defined in Tables I and II)

Subscripts

e = experimental
r = reference
s = smoothed
o = attenuation

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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