distance are $+2.6 \times 10^{-5}$ A./°C. for fluid 8515 from 65° to 177°C. and $+8.2 \times 10^{-5}$ A./°C. for fluid 5606 from 30° to 177°C.

ACKNOWLEDGMENT

The choice of the experimental method and construction of part of the equipment were due to the efforts of R. E. Ramsay.

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Received for review January 6, 1958. Accepted May 3, 1958.

Thermal Conductivities of Aviation Hydraulic Fluids

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In recent years, considerable attention has been given to the field of thermal conductivity. Several investigations have been particularly fruitful in revealing theoretical and empirical correlations (*6, 17, 18*). However, an accurate knowledge of heat conductivity must still come from experimental investigation. This is especially true in the case of hydraulic fluids, which are mixtures of different and sometimes unusual compounds. Hydraulic fluid conductivities need to be well defined as these values are critical in the design of heat exchangers for modern aircraft.

Hydraulic Fluid MIL-0-5606 is being used extensively in aircraft at the present time. It is a petroleum-base fluid with a polyalkylmethacrylate thickener. Oronite High Temperature Hydraulic Fluid 8200 is composed predominantly of a specific disiloxane derivative with a silicone thickener (*8*). Oronite High Temperature Hydraulic Fluid 8515 is essentially the composition of Fluid 8200, except that it contains 15% by weight of di(2-ethylhexyl) sebacate (*8, 22*).

APPARATUS

The filament method of measuring thermal conductivity was used because of its simplicity and precision. The basic design of the filament cells was essentially that of Langstroth and Zeiler (*13*). Figure 1 shows a typical cell.

The dimensions of the filament cells are listed in Table I. The wire diameter of the finely coiled tungsten filament was approximately 0.023 cm. (*13*). The resistance of each filament was about 26 ohms at 25°C. The change of cell resistance with temperature was found experimentally to be a linear function of temperature from 25° to 200°C.

Two systems were used for thermostating the filament cells. For temperatures up to 75°C., and 18-quart water bath with an infrared heater controlled by a mercury regulator was used (Arthur H. Thomas Co., Philadelphia, Pa.). At temperatures above 75°C., a 9-quart stainless steel beaker filled with a high-flash-point oil was used as the constant temperature bath. The beaker was insulated on the side and bottom by several inches of loosely packed asbestos. The top was covered by a plate of 1/8-inch Transite. A constant temperature was maintained by a 500-watt heater working off a Thermotrol temperature regulator (Hallikainen Instrument Co., Berkeley, Calif.).

The oil was circulated by an efficient hollow-blade

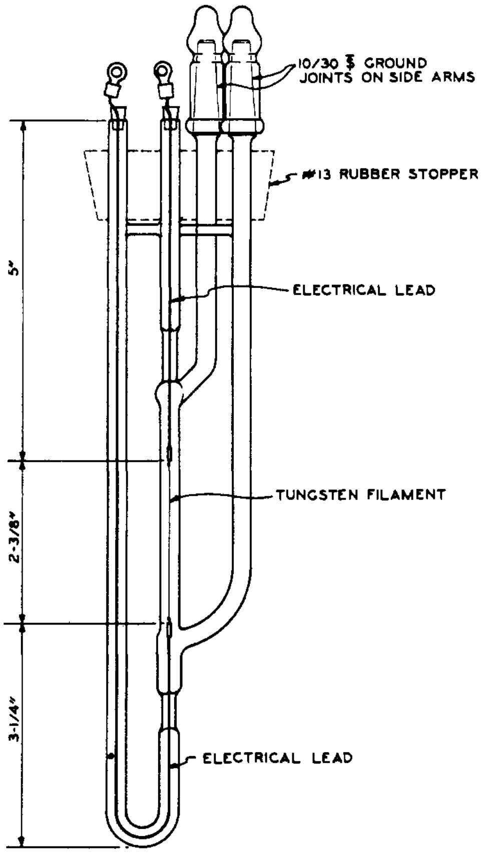

Figure 1. Filament cell

Table I. Characteristics of Filament Cells

Filament Cell Number	External Radius, Inch	Internal Radius, Inch	Filament Length, Inches	Change of Cell Resistance with Temperature, Ohm/° C.
1	0.245	0.162	1.76	0.1071
2	0.294	0.204	1.71	0.1092
3	0.197	0.128	2.02	0.1145
4	0.238	0.155	1.80	0.1140
5	0.294	0.204	2.20	0.1092

stirrer. Temperatures were read to 0.1°C. from a mercury-in-glass thermometer calibrated against a platinum resistance thermometer certified by the Natural Bureau of Standards.

A schematic diagram of the electrical circuit is shown in Figure 2. The variable arms of the Wheatstone bridge were composed of decade resistance dials. In addition, the rheostat arm had a 0.010-ohm plugboard graduated in units of 0.001 ± 0.0001 ohm. A standard 12-volt auto battery served as the power source. The potentiometer was a Leeds and Northrup Model 8662 portable indicator, and the galvanometer was a Leeds & Northrup Model 2430.

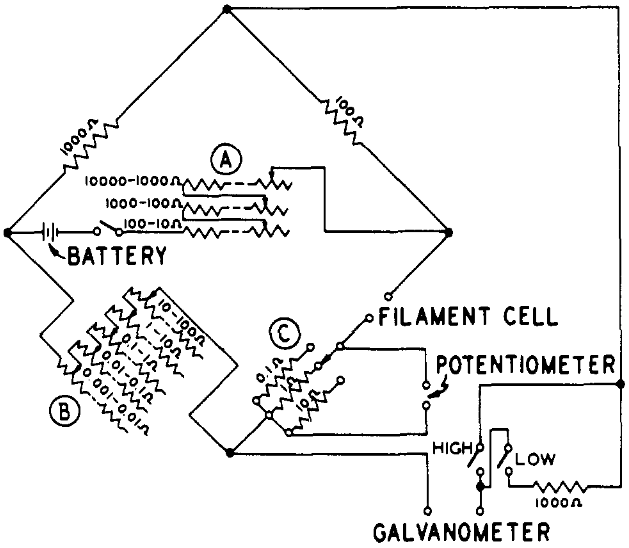

Figure 2. Electrical diagram of Wheatstone bridge

PROCEDURE

Before initial use, the cells were cleaned by passing 8*N* nitric acid through the annular space. After several washings with distilled water, the cells were air-dried and then rinsed twice with the test fluid. Dry nitrogen gas was bubbled through the system and the test liquid for several minutes to remove traces of oxygen. Then, the filament cells were filled, capped, and placed firmly and vertically in the bath. The cells required about 10 minutes in the bath to come to thermal equilibrium.

By adjusting the resistances at *A* in Figure 2, a constant current of about 5 ma. was passed through the test cell. The current was measured indirectly from a potentiometer which gave the voltage drop across a standard, 1-ohm resistor at *C*, Figure 2. The cell resistance at balance was measured at *B*. A 1-place interpolation by measuring galvanometer swings gave resistances to 0.0001 ohm. The true cell resistance was obtained by subtracting from this value the variable arm resistance obtained by shorting out the cell leads close to the filament. The measurement of current and cell resistance was made at 8 to 11 different settings on *A* and covered about a tenfold range of power input. Using the criterion of constant filament resistance, it was found that 6 minutes was adequate time for reaching equilibrium at successive power settings. Check periods of an additional 6 minutes were used after each measurement to check for the presence of transient changes in resistance and bath temperature. Data at each temperature were taken in order of increasing power input.

Values for thermal conductivity, *k*, were calculated from Equation 1, which is equivalent to expressions presented by others (*6*, *13*).

$$k = \frac{A}{m - B} \qquad (1)$$

$$A = \frac{\ln(r_l/r_f)}{4.185 \times 2\pi L} \times \frac{R_f - R_e}{T_f - T_e} \; \frac{\text{cal. ohm}}{\text{joule cm. °C.}} \qquad (2)$$

$$B = \frac{\ln(r_e/r_l)}{4.185 \times 2\pi L \; k_g} \; \frac{R_f - R_e}{T_f - T_e} \; \frac{\text{ohm sec.}}{\text{joule}} \qquad (3)$$

The terms *A* and *B* have been modified to include the changes in borosilicate glass conductivity and cell resistance with temperature. The thermal conductivity of borosilicate glass from room temperature to 250°C. is given by Equation 4 (*25*).

$$\frac{k_g \text{cal.}}{\text{cm. sec. °C.}} = 0.00245 \log T°_K - 0.00352 \qquad (4)$$

The values of *A* and *B* are dependent on the dimensions of the filament cell. The temperature coefficients of thermal expansion for tungsten and borosilicate glass have no appreciable influence on cell dimensions. The factor *A* is difficult to determine directly because the effective radius of the finely coiled tungsten filament is not readily measured. Therefore, *A* was calculated from Equation 1 by using data on liquids of known conductivity. Dimensions in Table I and Equation 4 were used to calculate *B*. These dimensions are sufficiently accurate because *B* is only a small fraction of *m*.

To derive conductivity values, the only experimental unknown is *m*, the change of cell resistance with power input. An approximate slope can be obtained by drawing a line through the plotted data. A more precise value from each slope came from least squares analyses.

EXAMINATION OF ERROR

The most serious errors involved in measuring thermal conductivity are the various sources of heat loss. Theory requires that heat from the filament be dissipated only through the liquid and there by conduction alone. The principal possibilities for deviation from ideality are discussed below.

Convection. In these experiments, no evidence of convection was found, as linear plots of cell resistance *vs.* power input were achieved with cells of different dimensions and at the highest temperature of investigation. Several factors minimized this possible source of error. The viscosity decrease with temperature for the fluids tested is low (*8*). The thickness of the test fluid in the annular space was relatively small (*13*), the imposed temperature differences did not exceed 1°C., and the cells were mounted vertically and were essentially vibration free (*9*, *20*). It has been shown that theory alone is not sufficient to determine the contribution of convection (*20*).

Radiation. The ratio of heat radiated to heat conducted should be less than 2% (*24*), although the effect does increase with temperature (*14*). The small temperature differentials on the test liquid (*23*), the small diameter af the tungsten filament, and an unknown amount of radiant energy which is absorbed by the test liquid all reduce the contribution of radiation. Therefore, no correction was made.

Resistance. Experimental results are computed directly from filament resistance. Therefore, spurious and transient resistance changes are a possible source of error. These errors may be due to changes in contact resistances and slight drifts in the temperature of the thermostated bath. Consistent errors were corrected by comparing data with a reference linear plot of resistance versus temperature for each cell. Errors due to fluctuations in resistance were compensated by measuring resistance changes during the check periods of 6 minutes. These 6-minute test periods followed the 6 minutes allowed for thermal equilibrium at each successive power input.

Miscellaneous. The magnitude of heat losses due to conduction along the filament leads is less than 0.4% of the power input for an apparatus of similar design (*13*). No correction has been entered as the error is further reduced by the use of calibrating standards.

During construction, each filament was visually aligned within the borosilicate glass tube. The careful centering of the filament eliminated a possible source of error in conductivity data (*16, 26*).

Heat losses due to evaporation of the test liquid were negligible. This was indicated by the low vapor pressures of the hydraulic fluids at temperatures of study (*8*) and the lack of liquid condensation in the cool portions of the cells outside the thermostat.

Table II. Thermal Conductivities of Aviation Hydraulic Fluids

Oronite High Temperature Hydraulic Fluid 8200			Oronite High Temperature Hydraulic Fluid 8515			Petroleum-Base Aircraft Hydraulic Fluid MIL-0-5606		
°C.	Cell	k^a	°C.	Cell	k^a	°C.	Cell	k^a
25.0	2	33.73	25.0	1	35.4	25.0	1	30.0
25.0	1	33.10	25.0	2	36.4	25.0	2	29.3
50.0	1	31.89	60.0	1	32.5	52.2	3	27.1
50.0	1	32.16	60.0	2	31.1	65.0	1	25.7
50.0	2	32.46	81.0	3	32.1	65.0	2	25.2
50.0	2	33.02	81.0	4	30.0	80.6	3	25.3
73.0	1	31.48	90.1	1	30.1	81.6	4	24.5
73.0	2	30.50	90.1	2	30.7	95.0	1	25.0
85.0	1	28.88	90.1	2	31.6	95.0	2	23.3
85.0	2	29.89	99.8	3	30.9	97.3	4	25.1
99.2	5	28.48	105.7	4	29.9	111.0	3	23.6
99.7	1	27.27	109.7	4	27.8	112.4	4	24.4
130.2	1	27.11	130.1	4	29.3	140.8	3	22.8
159.8	1	23.94	131.4	3	28.9	151.5	1	19.2
169.1	5	22.47	141.2	4	26.7	171.3	3	19.2
			160.4	3	26.1			
			160.8	5	28.0			
			162.7	4	26.8			
			189.1	3	26.6			

[a] Thermal conductivity in calories/cm. second °C. × 10^5

All measurements were made essentially at 1 atmosphere pressure as the caps of the filament cells were kept loose. Errors due to changes in atmospheric pressure should be negligible as thermal conductivities change only slightly with pressure (*4*).

Thermal conductivities measured by the filament method depend upon efficient thermostating of the cells. As evaluated by changes in filament resistance, the greatest deviations in temperature were about ±0.01°C. and occurred at the highest temperatures of study. The efficiency with which the thermostated bath could be controlled dictated both the precision and the upper temperature limit of thermal conductivity measurements.

RESULTS

The thermal conductivities of three aviation hydraulic fluids have been measured over a wide range of temperatures. The conductivity values at atmospheric pressure are shown in Table II. Results were derived from data on five different filament cells and are based on two thermal conductivities taken as standards (*6*): methanol, 50.5×10^{-5} cal./cm. second °C. at 25°C.; and 1,2,4-trichlorobenzene, 26.7×10^{-5} cal./cm. second °C. at 81°C. The value chosen for methanol may be several per cent high (*15*). The results of this research appear to indicate that the value chosen for methanol at 25°C. is about 3% high relative to that for 1,2,4-trichlorobenzene at 81°C. The thermal conductivity of 1,2,4-trichlorobenzene has not been widely investigated. In calibration, equal weight was given to the two standards. Subsequent research on these liquids may require small and easily made adjustments in experimental values.

Figures 3 through 5 show the change of thermal conductivity with temperature for each hydraulic fluid. The best line from a least squares calculation is drawn in, and dotted lines indicate the 95% confidence limits or ±2 standard deviations. A mathematical interpretation of experimental data indicates that, over the temperatures of investigation, the thermal conductivities of these fluids may be best expressed as a linear function of temperature (*12*). Therefore, conductivities at desired temperature, k_t, are given in the form:

$$k_t = k_a\,[1 + \alpha\,(t - t_a)] \pm s \qquad (5)$$

By using the c.g.s. units in Table III, thermal conductivities can be calculated in units of

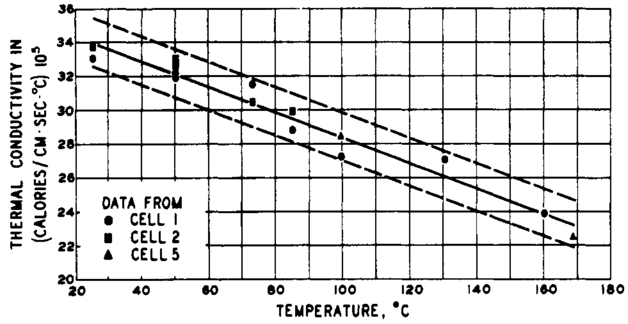

Figure 3. Oronite high temperature hydraulic fluid 8200
— — — — 95% Confidence limits

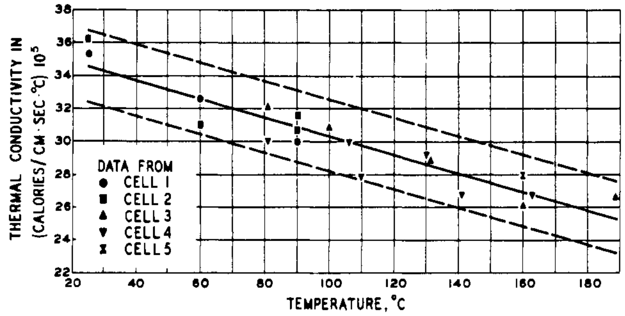

Figure 4. Oronite high temperature hydraulic fluid 8515
— — — — 95% Confidence limits

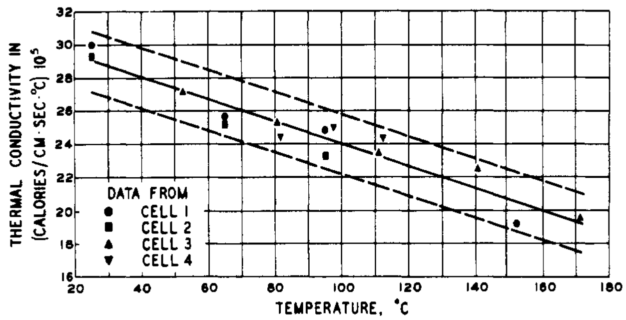

Figure 5. Aircraft hydraulic fluid MIL-0-5606
— — — — 95% Confidence limits

Table III. Conductivity Values for Equation 5

		Fluid 8200	Fluid 8515	Fluid MIL-0-5606
Experimental temperature range	°C.	25–169	25–189	25–171
	°F.	77–336	77–372	77–340
Factors Equation 5 in c.g.s. units	k_a	29.8×10^{-5}	30.1×10^{-5}	24.7×10^{-5}
	α	-2.53×10^{-3}	-1.90×10^{-3}	-2.69×10^{-3}
	t_a	81.6	104.9	91.24
	s	0.70×10^{-5}	1.1×10^{-5}	0.92×10^{-5}
Factors Equation 5 in engineering units	k_a	0.0720	0.0727	0.0596
	α	-1.41×10^{-3}	-1.06×10^{-3}	-1.49×10^{-3}
	t_a	178.8	220.8	196.2
	s	0.0017	0.0026	0.0022

$$\frac{\text{Calories cm.}}{\text{Sq. cm. second °C.}} = \text{cal./cm. second °C.}$$

The engineering units will give thermal conductivities in

$$\frac{\text{B.t.u.} \times \text{feet}}{\text{Sq. ft. hour °F.}} = \text{B.t.u./ft. hour °F.}$$

Sometimes compilations report data in terms of $\Delta k/\Delta T$, the change of thermal conductivity with change in temperature. The results in this simpler form appear in Table IV.

Table IV. Change of Thermal Conductivity with Temperature

Fluid	In $\frac{\text{Cal. Cm.}}{\text{Sq. Cm. Second °C.}}$/°C.	In $\frac{\text{B.t.u. Ft.}}{\text{Sq. Ft. Hour °F.}}$/°F.
5606	$-(0.0662 \pm 0.0058) \times 10^{-5}$	$-(0.0000890 \pm 0.0000078)$
8200	$-(0.0753 \pm 0.0042) \times 10^{-5}$	$-(0.000101 \pm 0.000057)$
8515	$-(0.0572 \pm 0.0056) \times 10^{-5}$	$-(0.0000769 \pm 0.0000075)$

STATISTICAL ANALYSIS

Least squares analyses were obtained from a Datatron electronic calculator for each experimental slope. Data indicate that, on the average, the resultant conductivity values have a probable error of ±2.0%. Least squares analyses on thermal conductivity *vs.* temperature data indicate an average probable error for each conductivity value of ±3.2% in the range 19 to 35 c.g.s. units. This signifies that, in addition to slope deviations, there is an unspecified error which contributes to the spread in results. The undefined error represents the maximum possible error in cell calibrations and is due at least in part to this factor.

It has been common in the literature to estimate error on the basis of variables in a single apparatus and from results at only one and two temperatures. Such interpretations are likely to be in error, as indicated by the statistical evaluation of data from this research.

DISCUSSION

Hydraulic Fluid 8200 has a thermal conductivity at 28°C. of 33.8×10^{-5} cal./cm. second °C. Various silicone fluids, as well as substituted silanes, have reported conductivities both above and below this value (*1, 3, 10*). Tetraalkyl silicates have thermal conductivities in the range 30 to 32×10^{-5} c.g.s. unit at room temperature (*2, 6*).

Fluid 8515 has the composition of 8200, except that it contains 15% by weight of di(2-ethylhexyl) sebacate (*8, 22*). The thermal conductivity for the diester has been reported from 28° to 220°C. (*5*). The measured thermal conductivity of Fluid 8515, at all temperatures, is less than that of the sebacate ester, yet slightly higher than the thermal conductivity of Fluid 8200. Assuming the approximation of weight additivity for thermal conductivity, the calculated and measured values for Fluid 8515 differ by 1.5, 3.3, and 6.5% at 50°, 100°, and 150°C. The agreement is thus quantitative, within the precision of method at 50° and 100°C.

The thermal conductivity of petroleum-base fluid 5606 at 25°C. is 29.0×10^{-5} c.g.s. unit. This value differs by only a few per cent from conductivities reported at room temperature for paraffin, mineral, and heat transfer oils (*11, 21, 23*). The thermal conductivity temperature coefficients reported in this paper are larger than most literature values for similar liquids (*19, 21*). This indicates that the high temperature conductivity results are relatively lower than similar data obtained by other investigators. Low results in filament cells are improbable, although they can arise from air bubbles in the cell or other unsuspected hindrances to heat flow. Positive errors at elevated temperature are much more probable, as work at high temperature accentuates the many possible sources of heat loss.

The change in conductivity with temperature reported for Fluid 8200, if in error, is probably high, as the filament cell which generally gave the smallest coefficient was not used on this fluid. However, experimental data agree with the prediction that the conductivity temperature coefficient for Fluid 8200 should be larger than for Fluid 8515. This is because Fluid 8515 contains di(2-ethylhexyl) sebacate, which has a temperature coefficient less than that of Fluid 8200 (*5, 6*).

ACKNOWLEDGMENT

W. R. Doty and V. C. Davis were responsible for construction of the filament cells and the Wheatstone bridge.

NOMENCLATURE

k = heat or thermal conductivity
k_a = thermal conductivity at average temperature investigated t_a
k_g = thermal conductivity of borosilicate glass
k_t = desired conductivity at temperature t
L = filament length
m = slope of filament resistance versus power input to cell in ohms second per joule
r_e = radius of external wall of borosilicate glass cell
r_f = radius of filament
r_i = radius of internal wall of borosilicate glass cell
R_e = filament resistance at temperature T_e
R_f = filament resistance at temperature T_f
s = standard deviation of experimentally measured thermal conductivities
t = test temperature
t_a = average temperature of investigation
T_e = temperature of external wall of borosilicate glass cell
T_f = filament temperature
α = temperature coefficient of thermal conductivities

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Received for review August 30, 1957. Accepted April 7, 1958. Division of Petroleum Chemistry, 132nd Meeting, ACS, New York, N. Y., September 1957.

Specific Heat of Biphenyl and Other Polyphenyls. Correlation of Specific Heat Data for Phenyl Type Compounds

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The increasing applications for heat transfer media at high temperatures have created a greater demand for high temperature physical property studies of various materials. In recent years, several groups of investigators at this laboratory have been involved with precise measurements of various physical properties, such as viscosity, surface tension, thermal electromotive force, thermal conductivity, heat transfer coefficients, and specific heat on substances of interest as heat transfer media.

The specific heat of biphenyl, metaterphenyl, metaquaterphenyl, and the polymer-biphenyl mixture was measured as part of a program concerned with organic coolants. The program involved heat transfer studies (measurement of heat transfer coefficients, fouling, and polymerization effects on heat transfer) in a pumped loop, and investigation of the physical properties of these coolants.

EXPERIMENTAL

The apparatus has been described (*6*) in some detail. Briefly, the calorimeter is a modified version of Southard's apparatus (*5*), in which the drop method is utilized. The sample is dropped at a known temperature into the calorimeter which measures the heat evolved from the furnace temperature to the operating temperature of the calorimeter (86°F.). The heat capacity is then derived from the enthalpy measurements by the usual methods.

The samples were vacuum sealed in Type 304 stainless steel buckets, which were calibrated in the calorimeter system over the desired temperature range (200° to 600°F.). The weights, in vacuo, of the samples and the containers are as follows:

Biphenyl	8.2130 grams
Type 304 S.S. container	22.9605 grams
Metaterphenyl	8.7157 grams
Type 304 S.S. container	23.8820 grams
Biphenyl polymer	7.9917 grams
Type 304 S.S. container	23.0524 grams
Metaquaterphenyl	7.7731 grams
Type 304 S.S. container	23.0059 grams

The heat content results for biphenyl and metaterphenyl are listed in Table I. The heat content results for the loop polymer and the metaquaterphenyl are not included, because a supercooling effect was evident in each. Therefore, the values determined do not represent the true heat contents of the materials, as the heats of fusion, ΔH_f, were not recorded. To obtain these heat values, runs would have had to be extended over a considerable period of time (several hours), and possibly this would introduce additional error and actually add very little data. The enthalpy equations for biphenyl and metaterphenyl in engineering units are as follows:

Table I. Heat Content of Biphenyl and Metaterphenyl

Temp., °F.	$H_t - H_{86}$, B.t.u./Lb. Obsd.	Calcd.	% Deviation Calcd.-Obsd.
	Biphenyl		
204.89	97.39	97.58	+0.19
205.92	98.22	98.03	−0.19
421.56	200.02	201.24	+0.61
423.16	202.08	202.07	0.00
423.64	203.51	202.32	−0.59
577.90	285.73	285.89	+0.06
578.14	286.20	286.02	−0.06
			Mean ±0.24
	Metaterphenyl		
215.89	87.62	88.04	+0.48
216.75	88.97	88.42	−0.62
421.93	184.71	184.97	+0.14
422.29	185.42	185.15	−0.15
581.92	269.62	270.00	+0.14
581.92	270.40	270.00	−0.15
			Mean ±0.28

Table II. Heat Capacity of Biphenyl, Biphenyl-Tar, Metaterphenyl, and Metaquaterphenyl

Temp., °F.	Cp B.t.u./Lb. °F. Obsd.	Calcd.	% Deviation Calcd.-Obsd.	Cp Monsanto (*3*)	% Deviation Monsanto-Obsd.
			Biphenyl		
314.1	0.479	0.479	0.0	0.473	−1.3
391.7	0.505	0.505	0.0	0.508	+0.7
500.4	0.542	0.542	0.0	0.558	+2.9
			Biphenyl-Tar (60% Biphenyl, 15% Terphenyls, 25% Higher Polymers)		
312.2	0.470	0.468	−0.5	0.464	−1.3
393.2	0.496	0.495	−0.3	0.501	+0.9
501.3	0.531	0.531	+0.1	0.550	+3.5
	Metaterphenyl				
318.4	0.470	0.470	0.0		
399.1	0.497	0.497	0.0		
502.0	0.531	0.531	+0.1		
	Metaquaterphenyl				
316.9	0.466	0.466	0.0		
395.0	0.490	0.490	0.0		
501.6	0.523	0.523	0.0		