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# Specific Heats of Aviation Hydraulic Fluids

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It is useful to know the specific heats of hydraulic fluids over wide temperature ranges. For the severe conditions under which such fluids perform in modern supersonic aircraft, specific heat is quantitatively considered in heat transfer calculations in aircraft design. It is instrumental in determining rates of heating or cooling under unsteady state conditions. The choice of a hydraulic fluid with a given specific heat will thus influence the transient thermal response characteristics of the hydraulic system and will partially define its thermal performance.

Empirical correlations have proved very satisfactory for predicting the specific heats of the common pure liquids and of certain liquid mixtures (*9, 15, 20*). Unfortunately, estimating specific heats of common hydraulic fluids by this approach is very difficult. First, fluids are often compounded from substances of greatly differing molecular type. This results in large heats of mixing and makes unreliable any additive rule for predicting specific heats of fluids from their pure components. There is a dearth of heat capacity data on liquids which are chemically related to the components in many hydraulic fluids. Moreover, the few available values are not in good agreement and do not generally cover a large temperature range.

Therefore, it is necessary to evaluate the specific heats of the hydraulic fluids experimentally.

## HYDRAULIC FLUIDS

The three hydraulic fluids investigated are not pure compounds but mixtures compounded for unique and desirable properties (*5*). Aircraft hydraulic fluid MIL-0-5606 is a petroleum base fluid which is recommended for use below 70°C. To date, over 25,000,000 gallons of this fluid have been placed in operation. A typical composition of this fluid is shown in Table I.

Oronite high temperature hydraulic fluid 8200 was developed to provide a fluid with excellent physical properties for use in aircraft at elevated temperatures. The fluid is composed predominantly of a specific alkoxydisiloxane. It contains a silicone thickener which acts as a viscosity index improver.

**Table I. Composition of Fluid MIL-0-5606**

| | Wt. % |
|---|---|
| Highly treated light gas oil fraction | 60–80 |
| Highly treated heavy gas oil fraction | 15–30 |
| Polyalkylmethacrylate | 4–8 |
| Oxidation inhibitors | 0.1–0.5 |
| Red dye | Trace |

Oronite high temperature hydraulic fluid 8515 has essentially the same composition as fluid 8200, except that it contains 15% by weight di(2-ethylhexyl) sebacate. This gives fluid 8515 a greater compatibility with rubber in hydraulic systems over the recommended operating range of –54° to 204°C.

## METHOD

A differential heating method was chosen for measuring specific heats. This choice was based on the nature of the hydraulic fluids, the wide temperature range over which results were desired, and the ease with which measurements can be made by this method. Differential heating techniques have received relatively little attention in the literature, although a simple and successful method based on this approach has been developed by Spear (*16*). The equipment used in this research was very similar to that of Spear. However, modifications were made; and it is felt that the additional contributions of this work have made the technique more workable and accurate.

In a differential heating method, results are obtained by comparing the rates of heating for a test liquid with that for a fluid of known specific heat. The conditions for heating the two fluids are made as nearly identical as possible. The liquids are contained in light metal vessels which are suspended in air jackets. They are then allowed to heat up in similar fashion towards the constant temperature of a surrounding bath. In such experiments, specific heat of the test liquid is calculated from the heat capacity of the reference fluid, the weights of the sample fluids, the thermal capacities of the two cells, and the times required for the cells to go through the same temperature interval. The value obtained is the mean specific heat of the fluid over a short temperature range.

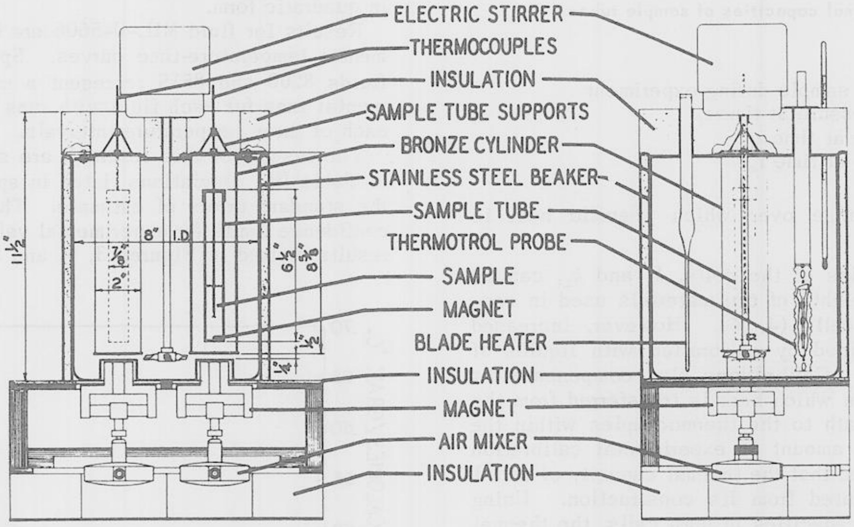

**Figure 1. Sections through constant temperature bath**

Figure 1 shows a diagram of the apparatus. The sample tubes are made of brass 1/16 inch in thickness, 7/8 inch in diameter, and 6½ inches in length. The tubes and their caps are nickel plated. It was necessary to build recesses 1⅝ inches in diameter and ⅞ inch in depth in the base of the liquid bath container directly opposite the bases of the brass cylinders. This permits the air-driven magnetic stirrers (Precision Scientific Co.) to be placed close enough to drive the magnets within the sample tubes. The force field of the magnetic stirrers is concentrated by using shaped bars of Armco iron. The liquid bath consists of Dow Corning 710 fluid stirred by a hollow-bladed stirrer. The bath is controlled by a Thermotrol temperature regulator (Hallikainen Instruments). Regulation is 0.01°C. from 25° to 220°C. Magnetic stirrer speed is measured by use of a Strobotac. The thermocouples are Chromel-Alumel. Their voltages are measured using a Leeds & Northrup White double potentiometer.

The liquid bath temperature is set at least 25°C. above the highest test temperature. The sample tubes are filled with 20 ml. of sample, weighed, and inserted in the constant temperature bath. For room temperature measurements, the sample tubes are precooled to slightly above the dew point of water before they are placed in the bath. As soon as the tubes are in the bath, a stethoscope is used to check the activity of the magnetic mixers. A prominent pinging sound is evidence of good mixer action. Voltages are recorded on each fluid at alternate minutes to the nearest microvolt. Temperature data are taken in this way from at least 15°C. below to 15°C. above each temperature at which the specific heat is desired. Sample tubes are reweighed at the end of the measurements.

Thermocouple voltages are converted to temperatures and plotted against elapsed times. The best line is drawn through the data, and the times required for the cells to pass through equal arbitrary temperature intervals are calculated. This temperature interval is from 12° to 28°C., depending on the rate of change of temperature with time. The test temperature is at the mid-point of the range. Usually, two intervals are evaluated at each test temperature. Several test temperatures may be calculated from one experimental run.

Specific heats are calculated from Equations 1 and 2 (*4, 16*).

$$\frac{k_1 + Cp_1\, W_1}{t_1} + R_1 = \frac{k_2 + Cp_2\, W_2}{t_2} + R_2 \tag{1}$$

where

$k_1$, $k_2$ = thermal capacities of cell 1 and cell 2
$Cp_1$, $Cp_2$ = heat capacities of liquids in cell 1 and cell 2
$W_1$, $W_2$ = weights of liquids in cell 1 and cell 2
$R_1$, $R_2$ = evaporation equivalence factors for cell 1 and cell 2
$t_1$, $t_2$ = times required for cell 1 and cell 2 to go through the same temperature range

Corrections for losses due to evaporation were necessary only for diphenyl ether above 180°C. The correction calculation was based on the following assumptions: that the heat loss is proportional to the product of the vapor pressure and the elapsed time, that heats of evaporation remain constant over the temperature interval, and that Trouton's rule is applicable. From the assumptions, *R* may be calculated as:

$$R = \frac{(\Delta H_v)(W_T)}{(P_f)(t_f)} \frac{[(t_b)(P_b) - (t_a)(P_a)]}{(t)(\Delta T)} \tag{2}$$

where

$\Delta H_v$ = heat of vaporization per unit weight

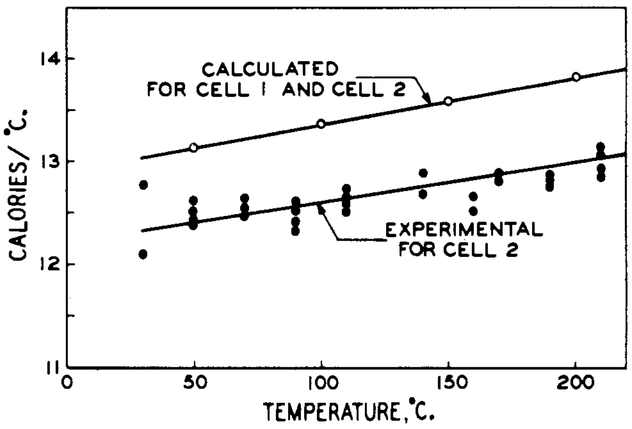

Figure 2. Thermal capacities of sample tubes

$W_T$ = weight loss of sample during experiment
$P_f$ = final vapor pressure at time $t_f$
$P_b$ = vapor pressure at time $t_b$
$P_a$ = vapor pressure at time $t_a$
$t = t_b - t_a$
$\Delta T$ = temperature range over which specific heat is calculated

The thermal capacities of the cells, $k_1$ and $k_2$, can be calculated from the weights of the materials used in constructing the sample cells (*4, 16*). However, increased accuracy can be obtained by calibration with liquids of known specific heats. Calibrations also compensate for variations in the way in which heat is transferred from the constant temperature bath to the thermocouples within the cells. To reduce the amount of experimental calibration required, it was assumed that the thermal capacity of cell 1 was correct as calculated from its construction. Using liquids of known heat capacities in both cells, the thermal capacity of cell 2 is then calculated from Equation 1. Results obtained in this way are shown in Figure 2. Over-all accuracy of the calibration was confirmed by observed consistent specific heat data for different weights of test sample and accurate results on fluids of known specific heat, examples of which are shown in Table II.

Water and heptane are used as standards in the region from 25° to about 30°C. below their respective boiling points. Diphenyl ether is used from 80° to 220°C. Values for specific heats of the standards are known to about ±0.2% (*6, 11*). Distilled water boiled to remove occluded gases was used. The diphenyl ether was a 25% center distillation cut from Eastman Organic Chemicals No. 104. Its freezing point was 26.77°C. Literature values (*18*) are 26.85° and 26.90°C. The heptane was also a center distillation cut of Phillips 99 mole % with a freezing point of −90.66°C., identical with the reported value (*1*).

Table II. Sample Accuracy Tests at 60°C.

| Reference Fluid | Test Fluid | Specific Heat |  | % Error |
|---|---|---|---|---|
|  |  | Calcd. | Correct |  |
| *n*-Heptane | *n*-Heptane | 0.573 | 0.569 | +0.7 |
| *n*-Heptane | Water | 0.997 | 1.000 | −0.3 |
| Diphenyl ether | Water | 0.997 | 1.000 | −0.3 |

## RESULTS

The specific heats of three hydraulic fluids have been measured by a differential heating method at atmospheric pressure from 25° to 220°C.

Results for fluid MIL-0-5606 and Oronite high temperature hydraulic fluid 8515 are best interpreted by linear equations relating specific heat and temperature. Data for Oronite high temperature hydraulic fluid 8200 show a marked increase in the change of specific heat with increasing temperature, and in consequence results are best presented in quadratic form.

Results for fluid MIL-0-5606 are based on three experimental temperature-time curves. Specific heat values for fluids 8200 and 8515 represent a minimum of six experimental runs for each fluid with runs made in duplicate over each of three temperature intervals.

The results of this research are shown in equation form in Table III. Deviations listed in specific heat values are the standard errors of estimate. These represent the 67% confidence limits for experimental values. The experimental results plotted in Figures 3, 4, and 5 show change of specific heat with temperature in metric units for each fluid. The best curve, as mathematically developed, has been drawn in. Dotted lines depict the 95% confidence limits or two standard deviations. In no case were discontinuities observed in temperature-time or specific heat-temperature curves. Therefore, no energetically important transitions occur within the three hydraulic fluids over the long temperature ranges of investigation.

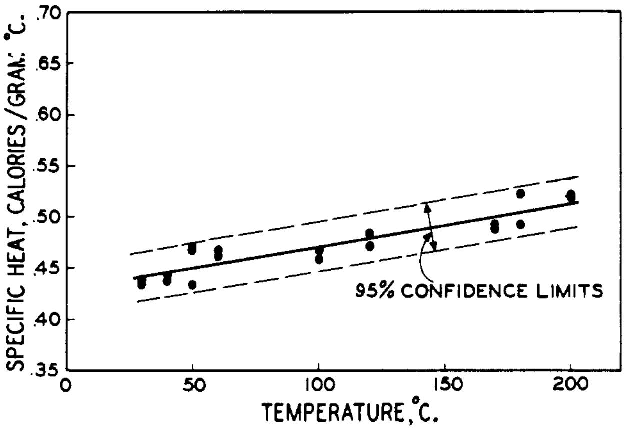

Figure 3. Specific heat of hydraulic fluid MIL-0-5606

The values measured on fluid 5606 agree well with values

Table III. Specific Heat Results

| Designation No. of Hydraulic Fluid | Temp. Range of Measurements |  | Specific Heats at Constant Pressure |  |
|---|---|---|---|---|
|  | °C. | °F. | Cal./gram °C., $T$°C. | B.t.u./lb. °F., $T$°F. |
| 5606 | 30–200 | 86–392 | $+0.430 + 4.16 \times 10^{-4}T_{^\circ\text{C.}}$<br>$\pm 0.012$ | $+0.423 + 2.31 \times 10^{-4}T_{^\circ\text{F.}}$<br>$\pm 0.012$ |
| 8515 | 25–220 | 77–428 | $+0.416 + 9.78 \times 10^{-4}T_{^\circ\text{C.}}$<br>$\pm 0.011$ | $+0.398 + 5.43 \times 10^{-4}T_{^\circ\text{F.}}$<br>$\pm 0.011$ |
| 8200 | 45–220 | 113–428 | $+0.365 + 6.76 \times 10^{-4}T_{^\circ\text{C.}}$<br>$+ 2.89 \times 10^{-6}T^2_{^\circ\text{C.}} \pm 0.013$ | $+0.354 + 3.18 \times 10^{-4}T_{^\circ\text{F.}}$<br>$+9.12 \times 10^{-7}T^2_{^\circ\text{F.}} \pm 0.013$ |

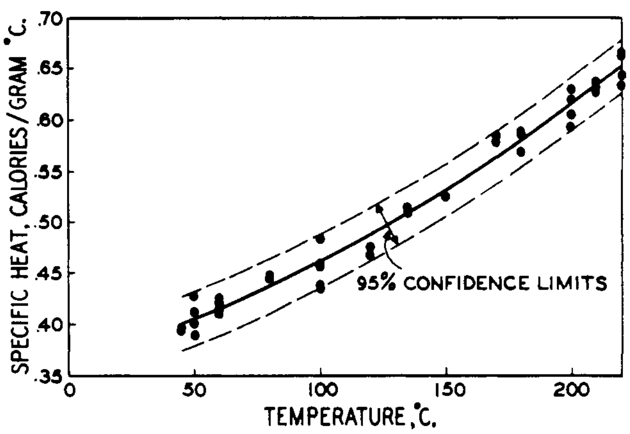

**Figure 4. Specific heat of Oronite high temperature hydraulic fluid 8200**

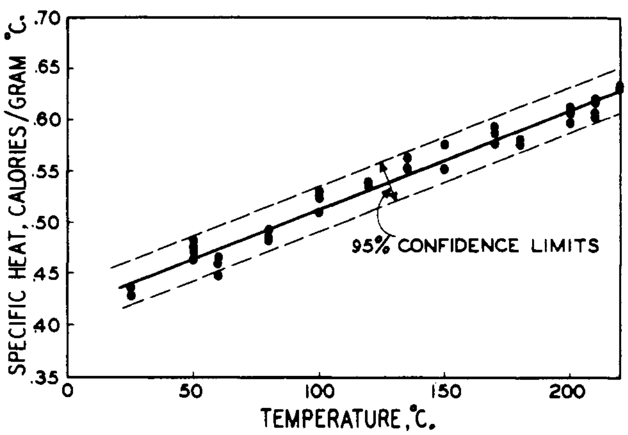

**Figure 5. Specific heat of Oronite high temperature hydraulic fluid 8515**

for a petroleum stock which is similar in composition and other physical properties (*20*). Results on the other two fluids are consistent with most of the data available on chemically related liquids (*2*, *16*), but they do not agree with estimated values (*5*) and should replace these approximate values for design purposes.

## DISCUSSION

Defining the specific heat for mixtures of dissimilar chemical types is a complex problem. The addition of an ester to a siloxane, as in the case of fluid 8515, is likely to produce a liquid mixture with large deviations from ideality. For such cases, both positive and negative deviations from specific heat additivity have been reported (*10*, *17*). However, prominent positive deviations in specific heat are far the most common result of mixing liquids of dissimilar type (*3*, *8*, *19*).

The specific heat of liquid di(2-ethylhexyl) sebacate has not been reported. Nonetheless, by considering specific heats of other esters it may be estimated that its value at room temperature should be considerably higher than that for fluid 8200 (*13*). Thus, by simple additivity the specific heat of fluid 8515 should be greater than that for fluid 8200. It is likely that the nonideality of the mixture in fluid 8515 adds further to its specific heat. This conclusion is substantiated by experimental results which show that at 60°C. the specific heat of fluid 8515 is 16% higher than that of fluid 8200. The two fluids differ only by 15% by weight of di(2-ethylhexyl) sebacate. Differences between the specific heats of di(2-ethylhexyl) sebacate and fluid 8200 and/or their heats of mixing must become less at elevated temperature. This is because the specific heats of fluids 8200 and 8515 become the same at about 190°C. Although positive deviations and maxima are often observed in specific heat versus composition curves for binary liquid systems, they do not generally represent compound formation or other unique phenomena.

A theoretical calculation of specific heats of liquid mixtures involves the use of partial molar quantities; but as they are obtainable only from specific heat data for the system in question, the method has little practical value (*8*).

In attempting to compare this work with previous investigations, it has been found that very few specific heats have been reported for liquids closely related to the components in fluids 8200 and 8515, per se, disiloxanes, silicones, and organic silicates (*2*, *12*, *16*). Among available values large discrepancies exist (*7*, *16*). Quantitative comparisons are further restricted because of the dearth of heat capacity data available on other hydraulic fluids. Bingham has cited experimental information on such fluids and reports hydraulic fluids types in order of decreasing specific heat: glycol-water base > castor base > petroleum base > phosphate ester base > silicone base (*2*). This general interpretation is probably valid at room temperature. However, this work on hydraulic fluids, which presents the first study over a long temperature range, indicates that Bingham's order will be altered at elevated temperature, because the specific heats of different fluids have widely different temperature coefficients.

The specific heat of a liquid may be calculated from data on the coefficient of expansion, isothermal compressibility, and speed of sound in the fluid (*7*). Density data, from which coefficients of expansion may be calculated, have been reported (*5*). Compressibility and speed of sound data have been made available but are as yet not in the regular literature.

A calculation based on these related quantities has led to specific heat values at 26.7°C. of 0.417 for fluid 8200 and 0.489 for fluid 5606. These results differ from extrapolated experimental values by ±7.9% and +10.6% for fluids 8200 and 5606, respectively. The agreement is good considering that values calculated are remarkably sensitive to errors in speed of sound and compressibility data.

Schiff's equation, Equation 3, for estimating specific heats of liquids has been tested on the three hydraulic fluids (*9*).

$$\rho \times Cp = 0.35 \tag{3}$$

where

$\rho$ = liquid density, grams per ml.
$Cp$ = liquid specific heat

For fluid 5606 the product of density and specific heat is constant at a value of 0.376 ± 0.002 over the full range of measurements from 25° to 200°C. Fluid 8200 yields a constant of 0.370 ± 0.005 from 45° to 60°C. Above this temperature and over the full experimental range for fluid 8515 the value for the constant is high and increases with increasing temperature.

Kardos has derived a theoretical equation involving specific heat (*14*).

$$Cp = \frac{k}{(U)(\rho)(L)} \tag{4}$$

where

$Cp$ = specific heat
$U$ = speed of sound in liquid
$\rho$ = liquid density
$L$ = available intermolecular distance
$k$ = liquid thermal conductivity

This equation may be solved for $L$, the effective intermolecular distance between molecules, as all other quantities have been experimentally measured. Intermolecular distances for the hydraulic fluids have been calculated over a range of temperatures. Values at 100°C. are 0.69, 0.66, and 0.57 A. for fluids 8200, 8515, and 5606, respectively. The temperature coefficients for intermolecular distance are +2.6 × $10^{-5}$ A./°C. for fluid 8515 from 65° to 177°C. and +8.2 × $10^{-5}$ 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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# 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

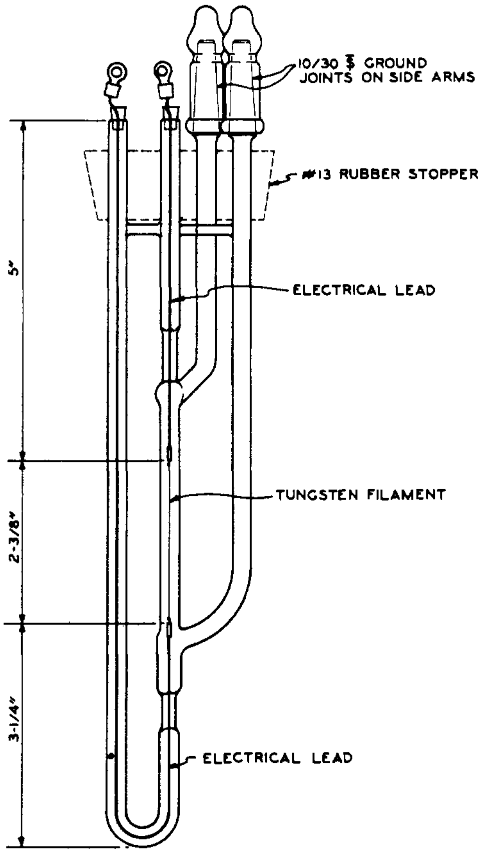

Figure 1. Filament cell

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 |