same charge distribution. We can therefore estimate that the entropy of $S_2O_7^{-2}$(aq) is about 58 cal. per degree mole.

Entropies of $Cr_2O_7^{-2}$(aq) and $S_2O_8^{-2}$(aq) are considerably greater than entropies of the more compact species SO_4^{-2}(aq) and CrO_4^{-2}(aq), which are more effective in orienting solvent dipoles because of their more concentrated charges.

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An Experimental Determination of the Thermal Conductivity of Several Greases

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MOST OF THE previous research efforts devoted to the determination of the properties and characteristics of greases have been concerned with lubricity, stability, and other properties directly connected with the use of greases as lubricants. Some work involved the microstructure of greases—the manner in which soap fibers are intermingled with oil. Vold (7) has examined the properties of soap itself, particularly thermal properties, such as thermal transitions (5).

An examination of the literature showed, however, that few results have been reported for thermal conductivity of greases. The purpose of this work was to measure the thermal conductivity of greases made from several different oils and soaps or solids as a function of temperature and soap content, and to relate the thermal conductivity of the grease to the thermal conductivities of the pure constituents.

EXPERIMENTAL APPARATUS AND PROCEDURE

Description of Apparatus. The apparatus was a guarded, steady-state, concentric cylinder cell with an annular space to contain the test sample. The cell included a central cylindrical bar broken lengthwise into three independent heater sections: a middle heater, and two guard heaters, one on either side of the middle heater. Each guard heater was separated from the middle heater by a Teflon (DuPont trademark) plug. The dimensions of the cell are shown in Figure 1.

This central bar was surrounded by an aluminum tube 11.26 inches long and 1.6500 inches in I.D. × 1.868 inches in O.D. leaving an annular space of 1.4975 inches in diameter and 1.650 inches in diameter for the sample. The outer aluminum tube and the central bar were concentrically aligned by means of Teflon spacers located at each end of the cell.

The middle heater and the two guard heaters were each constructed by tightly winding a glass-insulated, 24-gage constant wire into a spiral groove on the outside of a

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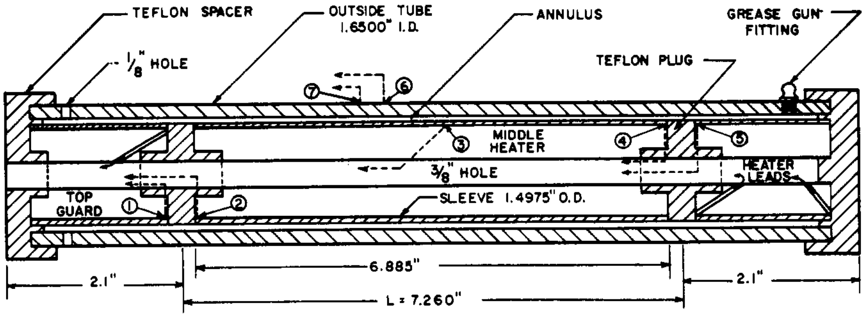

Figure 1. Drawing of conductivity cell

hollow aluminum bar. A tight-fitting aluminum sleeve (1.4975 inches in O.D.) was slipped over this winding so that this sleeve was in good thermal contact with both the heater wire insulation and the hollow aluminum bar. Copper heater leads were attached to the constantan heater wires and these leads extended from the cell through a ⅜-inch in diameter hole which ran through the center of the central bar. Copper-constant thermocouple junctions were located on the central bar on either side of each Teflon plug, between the plug and the end of the aluminum sleeve. Locations of thermocouples are shown as circled numbers (Figure 1). A glass insulated Chromel heater wire was wound into a spiral groove cut into the outside aluminum tube. Two thermocouple junctions were soldered into the wall of the outside tube. One end of the tube was setup with a grease gun fitting. Two ⅛-inch holes were drilled in the other end, diametrically opposite each other.

The outside heater and the two guard heaters used alternating current and were independently regulated by Powerstats (Superior Electric Co.). The middle heater used direct current so that its power could be measured with a standard resistor and direct current bridge circuit. The direct current was regulated with a decade box. A potentiometer (Leeds & Northrup K-2) was used for all voltage measurements.

The axial heat loss, from the middle heater, could be controlled by adjusting the current in each guard heater in order to give a small temperature difference across the Teflon plugs. This ensured that the heat generated in the middle heater was transferred only in the radial direction through the test sample in the annulus.

The thermal conductivity of the test material was calculated from measurements of the electrical energy input to the middle heater, the temperatures indicated by the thermocouples and the geometry of the cell.

The resistance of the middle heater was determined by comparing it with a National Bureau of Standards calibrated, secondary standard resistance in a bridge circuit using the K-2 potentiometer. The middle heater resistance, 4.410 ± 0.007 ohms, was the average of six measurements. This value was checked at higher temperatures and found to be independent of temperature.

Testing of Apparatus. The apparatus was first used to measure the thermal conductivity of glycerol. Table I shows the comparison between thermal conductivity measured with this apparatus and that of other workers (*8*). These values are the averages of several measurements with an experimental reproducibility of better than 2%.

The effect of axial heat loss across the Teflon plugs was determined experimentally by deliberately causing a temperature difference across one of the plugs, and observing the effect on measured values of thermal conductivity. With a difference as large as 2° F. across one of the Teflon plugs, the effect on the measured value of thermal conductivity was only 2%. The temperature difference across the Teflon plugs was usually controlled to less than 0.5° F.

To be sure that the grease sample would completely fill the cell annulus, a full size glass model of the cell was built and grease was pumped into its annulus. The grease completely filled the cell and no void spaces or air bubbles existed in the test section of the experimental apparatus. This model was also used to determine that no appreciable convection would occur in the cell, when thermal conductivity measurements were made on oils.

Experimental Procedure. Liquids were introduced, by means of a hypodermic syringe, into the annulus through holes at the top of the outside tube. Greases were pumped into the annulus through the grease gun fitting at the bottom of the cell (Figure 1). The inside heaters—the middle heater and the two guard heaters—were switched on. The outside heater Powerstat was set to give the desired, average temperature. After 2 or 3 hours, the guard heaters were adjusted so that there was very little temperature difference across either Teflon plug. Additional guard heater adjustments were made as necessary. After another 2 or 3 hours, the temperature differences across the Teflon plugs were about 0.1° to 0.5° F., and the average cell temperature was constant. When thermocouple voltages and the voltage drop across the standard resistances were constant for a period of 2 hours, the data established a thermal conductivity value. The average temperature of the sample was taken as the arithmetic average of the inside and outside temperatures.

Soap compositions were determined in the Port Arthur Laboratories, Texaco Inc., using ASTM procedures.

RESULTS

Thermal conductivity of grease as a function of soap composition, temperature, and conductivity of oil in the grease were measured for two sodium greases (6.5 and 12% soap by volume); two calcium greases (9.5 and 13.8% soap); three hydrocarbon oil–lithium greases (7.5, 14.2, and 17.2% soap); a clay thickened grease (10.0% clay) and a synthetic (silicone base) oil grease (20.5% lithium soap) and the respective oils used in these greases. Each of the calcium and sodium greases contained different oils, but the same oil was used in all three hydrocarbon oil–lithium soap greases. Grease conductivity was measured for one other calcium soap grease (13.0% soap). Measurements were made at temperatures from 100° to 300° F.

In general, the conductivities of the oil and greases decreased with increasing temperature. The grease conductivity decreased linearly with temperature at the same rate as the oil. The conductivity of each grease was higher than the conductivity of its oil. Experimental results are presented in Table II and in Figures 2 to 4, and general characteristics of the greases in Table III.

Table I. Comparison of Measured Values of Glycerine Conductivity

Temp. °F.	Thermal Conductivity, B.t.u./Ft.^{2}Hr.°F./Ft.		%
	(*8*)	This Work	Difference
137	0.161	0.154	4.3%
154	0.162	0.154	4.4%
160	0.163	0.156	4.3%

DISCUSSION

General Characteristics. The observed increase in thermal conductivity of a grease above that of its oil is expected because solid soap-type materials have thermal conductivities higher than those of hydrocarbon oils. The general trend to follow the temperature behavior of the oil would be expected, since the amount of solid added is relatively small, and because these solids have about the same thermal conductivity as the oil.

Effect of Soap. To explain the effect of soap or solids upon the thermal conductivity of a grease, some model of grease structure must be proposed. The simplest model would uniformly distribute the soap as clumps through the oil. Fricke (*3*) has shown that heterogeneous electrical conductivity depends upon the shape of the discontinuous phase and upon the relative magnitude of the conductivities of the pure constituents. For the case where the two conductivities differ by not more than a factor of 100, his result, solved explicitly for the conductivity of the soap, yields:

$$K_s = K_o\left[\frac{2(K_g - K_o) + V_s(K_g + 2K_o)}{K_o - K_g + V_s(K_g + 2K_o)}\right] \tag{1}$$

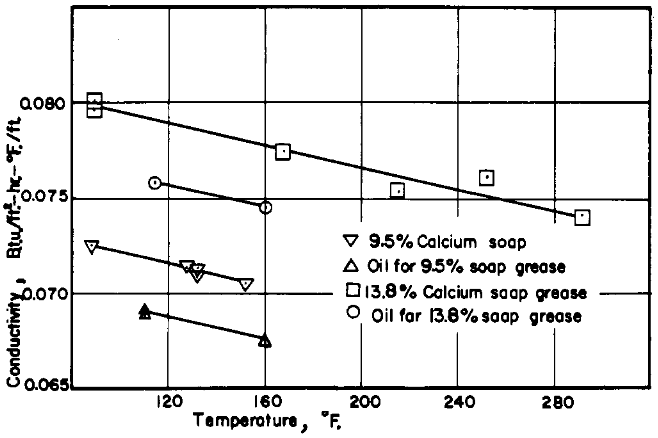

Figure 2. Calcium grease and oil conductivities

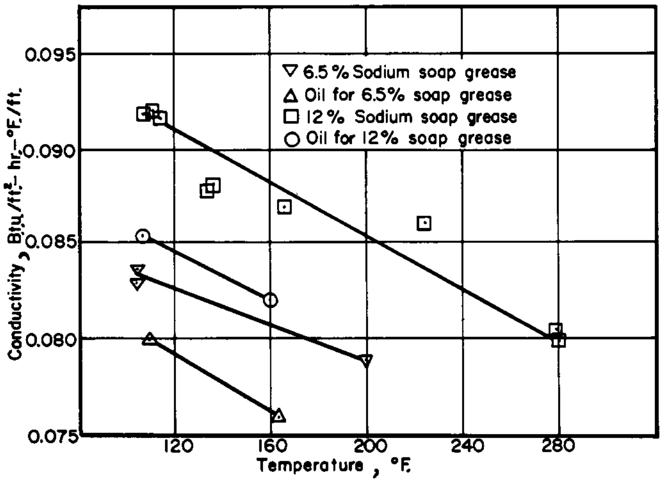

Figure 3. Sodium grease and oil conductivities

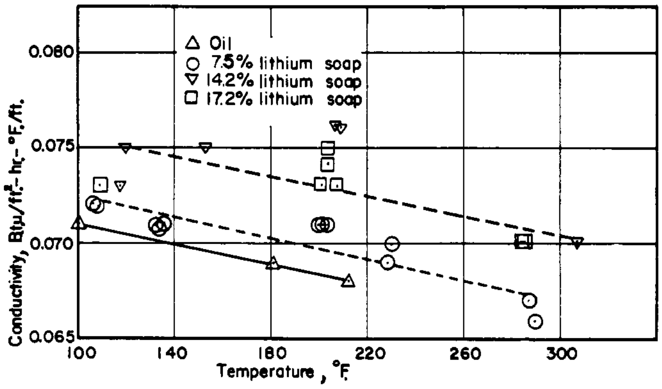

Figure 4. Lithium grease and oil conductivities

Upper dotted line is for 15% soap

Lower dotted line is for 7.5% soap

Table II. Conductivity of Greases and Oils

Percentage Soap	Temperature, °F.	Thermal Conductivity, B.t.u./Ft.²Hr.°F./Ft.
	Grease Contains Synthetic Oil and Lithium Soap	
20.5	88	0.0884
20.5	90	0.0880
20.5	90	0.0874
20.5	165	0.0876
Oil	115	0.0801
Oil	160	0.0797
	Calcium Grease[a]	
13.0	120	0.0760
13.0	120	0.0760
13.0	188	0.0750
13.0	215	0.0730
13.0	254	0.0720
	Clay Grease[b]	
10.0%[c]	92	0.0897
Oil	97	0.0714
Oil	210	0.0690

[a] Oil used in this grease was not measured. [b] Contained oil.
[c] Per cent clay.

Table III. Characteristics of Grease and Oil Samples

Grease	Soap, %	Identification
Calcium grease	9.5	Naphthenic oil from coastal crude, thickened with the calcium soap of animal tallow
	13.8	Solvent refined oil from mid-continent crude, thickened with the calcium soap of a hydrogenated vegetable fatty acid
	13.0	Naphthenic oil from coastal crude, thickened with the calcium soap of a hydrogenated vegetable fatty acid
Sodium grease	6.5	Paraffinic oil from mid-continent crude, thickened with the sodium soap of animal tallow
	12.0	Solvent refined paraffinic oil blend, thickened with the sodium soap of a coconut oil fatty acid
Lithium grease	7.5 14.2 17.2	Blend of solvent and nonsolvent refined oils from mid-continent crude and a naphthenic oil from coastal crude, thickened with the lithium soap of a hydrogenated vegetable fatty acid
Synthetic oil grease	20.5	Blend of a paraffinic oil from mid-continent crude and a synthetic oil, thickened with the lithium soap of mixed animal tallow and hydrogenated vegetable fatty oil
Clay grease	9.3	Blend of solvent and nonsolvent refined oils from mid-continent crude thickened with a hydrophilic clay rendered organophilic by a base exchange reaction

where K_s, K_o, and K_g are soap, oil, and grease conductivities respectively, and V_s is volume fraction of soap. K is conductivity in B.t.u./Ft.²Hr.°F./Ft. and V is the volume fraction, dimensionless.

Equation 1 applies to mixtures containing one phase dispersed discretely in another. Although electron microscope photographs show that greases contain intermingled soap fibers (*1, 6*) rather than discrete particles, they also indicate that the fibers tend to collect in clumps. Under polarized light at 100 × magnification, such apparently separate clumps appear (*4*). The precise character of the dispersion, as well as the shape of the particles, becomes of negligible importance as the conductivities of the mixed phases approach each other (*4*). Under the conditions encountered in a grease, the conductivity ratio is not more than 5 and Equation 1 should be entirely adequate for the estimation of the thermal conductivities of pure soaps.

Calcium Greases. The results for two greases and their respective oils are shown (Figure 2). The slopes of the lines for a grease and its oil are approximately equal. K_s was calculated, using Equation 1, for each calcium grease at

100° F. and found to be 0.11 B.t.u./Ft^{2}Hr.°F./Ft. The agreement is better than could be expected on the basis of the precision of the measured grease and oil conductivities. These are apparent soap conductivities and depend entirely on the validity of Equation 1. They are, however, consistent with values (*2*) for solids of this type.

Sodium Greases. The same general observations follow for sodium greases. The results for these greases are shown in Figure 3. Using Equation 1, the conductivity of the sodium soap was found to 0.16 B.t.u./Hr. Ft.^{2}° F./Ft. at 100° F. The remarks made concerning the accuracy and validity of the calcium soap calculations apply also to this case.

Clay Grease. The conductivity of the clay, calculated from Equation 1, was 1.10 B.t.u./Hr.Ft.$^{2\circ}$F./Ft. which could be compared to a value of 0.98 B.t.u./Hr.Ft.$^{2\circ}$F./Ft given by Forsythe (*2*).

Lithium Grease. These explanations apply as well to the results for the synthetic oil–lithium soap grease. The results for the hydrocarbon oil–lithium soap greases (7.5, 14.2, and 17.2% soap) did not follow as closely the simple behavior of the other greases. Figure 4 shows that the data for these greases scatter widely and that a higher conductivity was obtained for the 14.2% soap composition than for the 17.2% soap grease. This scatter and erratic behavior was observed during repeated determinations. Reproducibility would suddenly disappear even after a sequence of determinations had shown no effect on residence time, surrounding temperature, and reloading of the cell. The scattering is relatively small (about 7%), and the dash lines drawn in Figure 4 assume two soap compositions, 7.5 and 15%, and agree reasonably well with the prediction of Equation 1.

Effect of Grease Structure. A large variety of size, shape, and arrangement of the soap particles occurred among the greases studied. In some cases, greases of the same type would show quite different shapes—nearly spherical clumps in contrast to shardlike pieces. In all cases, the effect of the soap can be explained by Equation 1 as a simple composition effect. This implies that the character of the soap particles does not affect thermal conductivity. The thermal conductivity of the oils and soaps differs at most by a factor of 2; furthermore, most greases have a low soap content. Under these circumstances, the soap properties cannot be expected to affect the grease conductivity greatly. Measurements of thermal conductivity, therefore, would not characterize the structure of greases.

CONCLUSION

Thermal conductivity of greases is primarily determined by the thermal conductivity of the oils from which they are made. Thermal conductivity of a grease decreases with temperature at the same rate as its oil.

The effect of soap composition on the thermal conductivity of the greases can be determined by Equation 1 in terms of the conductivities of the pure soap and oil.

Thermal conductivity of greases is not sensitive to size or shape of the soap particles in the grease, and thermal conductivity measurements will not characterize the structure of greases.

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Critical Temperatures and Critical Pressures of Hydrocarbon Mixtures

Methane–Ethane–*n*-Butane System

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CONSIDERABLE experimental information on the critical temperatures and critical pressures of mixtures is presented in the literature. However, it is confined primarily to binary systems and complex mixtures of the natural gas type. Critical constants for systems lying between these two extremes are limited and for the most part have been obtained indirectly from vapor-liquid equilibrium studies. Rigas, Mason, and Thodos (*8*) present critical temperatures and critical pressures for four mixtures of the methane-propane–*n*-butane system. Price and Kobayashi (*5*) present vapor-liquid equilibrium data in the vicinity of the critical point for the methane-ethane-propane system, while Reamer, Sage, and Lacey are able to extract critical information from their vapor-liquid equilibrium data on the ternary systems, methane–*n*-butane–*n*-decane (*6*) and methane-propane–*n*-pentane (*7*) and Billman, Sage, and Lacey on the system methane-ethane–*n*-pentane (*1*).

To broaden the background involving these critical