probably not be considered significant if the discontinuity in frequency had not been so well established. It should be emphasized that the relative standard deviation in the case of a double amplitude of pressure fluctuation is much greater than the comparable information for the frequency and the mole fraction of the oxides of nitrogen.

The total experimental data yielded a standard error of estimate from the smooth curve at mixture ratios less than stoichiometric of 0.088 pound per square inch and at mixture ratios greater than stoichiometric of 0.193. For mixture ratios between unity and 1.10 there is a rapid increase in the standard error of estimate, which approaches a value of approximately 50 per cent of the average value at a mixture ratio of 1.08.

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Thermal Conductivity of Fluids. Nitrous Oxide

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A knowledge of the molecular thermal conductivity of nitrous oxide is important in predicting thermal transfer to this fluid under many of the conditions encountered in industrial practice. Available experimental information is limited. In this study, data concerning the thermal conductivity of nitrous oxide were taken at temperatures from 40° to 340° F. and at pressures up to 5000 pounds per square inch. Data near the critical state were not obtained due to the persistence of natural convection, even when the temperature gradients were small. The data show the normal trends in thermal conductivity with respect to variation in both pressure and temperature. No difficulty from thermal instability of the nitrous oxide was encountered.

IT IS NOT YET feasible to predict the molecular thermal conductivity of fluids at elevated pressures with an accuracy sufficient for engineering needs. Furthermore, experimental data are limited even for fluids of industrial importance. Keyes (*8*) recently made an excellent survey of the experimental data available for a number of gases. Sellschopp (*14*) and Vargaftik (*15*) studied the thermal conductivity of gases at high pressures, and Mason (*10*) reported the thermal conductivity of a number of liquids in the temperature range between 32° and 312° F.

Johnston and Grilly (*7*) and Eucken (*2*) measured the thermal conductivity of nitric oxide at atmospheric pressure, and Richter (*13*) investigated the effect of pressure and temperature upon the thermal conductivity of nitric oxide. Richter (*12*) also studied the thermal conductivity of nitrogen dioxide in the liquid phase at temperatures up to 160° F.

Experimental measurements of the thermal conductivity of nitrous oxide were reported by Keyes (*9*) for pressures up to 775 pounds per square inch at 122° F., and by

Johnston and Grilly (*7*) for atmospheric pressure. Johnston and Grilly also included a review of earlier data.

The present study was directed to measurements of the thermal conductivity of nitrous oxide at pressures up to 5000 pounds per square inch in the temperature interval between 40° and 340° F. It was not found practical to carry out these measurements in the vicinity of the critical state of nitrous oxide due to the persistence of natural convection, even when the temperature gradients were small.

APPARATUS AND METHODS

In principle, the thermal conductivity cell consisted of a metal sphere surrounded by a spherical shell which was separated from it by a small gap. The fluid under study was confined between the sphere and the surrounding shell. The complete assembly was mounted in an isothermal, agitated oil bath, and energy was supplied to the inner sphere by a uniformly mounted electrical heater. When a condition of steady state was achieved, the temperature difference between the surface of the inner sphere and of the shell was measured by thermocouples. From the measured rate of energy addition, the resulting temperature difference, and the equipment dimensions, the thermal conductivity could be calculated.

The apparatus used in the present work was a modification of that used in earlier studies (*12, 13*). The two spherical shells in the high pressure region were eliminated, and a new inner sphere 3.650 in. in diameter employed, which yielded a spherical sample thickness of 0.0173 in. when placed in the existing outer shell. The two spherical surfaces were lapped to within 0.0001 in. of a true sphere and were gold plated to reduce energy transport by radiation. The thermocouples were made from 0.003-in.-diameter copper and constantan wire and were electrically insulated from the cell. They were placed at the bottom of 0.0625-in.-diameter holes drilled perpendicularly to the surface and to within 0.050 in. of the surfaces of the inner sphere and outer shell. The thermocouples were arranged to measure differential temperatures directly or to measure temperatures relative to an ice bath. Two such differential thermocouples were mounted in the upper half sphere and four in the lower half. All other parts of the apparatus were as described earlier (*12, 13*).

The thermal conductivity was established from the relationship,

$$k = \frac{(\underline{q}_m/d\theta)(r_o - r_i)\phi_A}{4\pi r_o r_i (t_i - t_o)} - k_r - k_s \qquad (1)$$

which had been developed earlier (*12, 13*). During operation the energy loss through the supporting stem of the inner sphere was held to a negligible value by use of a guard heater. The coefficient of thermal transport by radiation was established from the Stefan-Boltzmann law. The energy transport by radiation did not exceed 0.5 per cent of the total transport at any state in the present work.

The measured temperature difference, Δt_m, was not the true temperature difference $(t_i - t_o)$ across the sample, but included the temperature changes between the metal surfaces and the thermocouple junctions. Since all energy transport within the metal was by conduction, the measured and actual temperature differences across the sample can be related by

$$(t_i - t_o) = \Delta t_m - \frac{(\underline{q}_m/d\theta)}{\beta} \qquad (2)$$

where $1/\beta$ is the thermal resistance for a particular thermocouple.

At elevated pressure there were small changes in the dimensions of the cell. Using the known mechanical properties of the steel, a correction factor to the dimensions, K_p, was derived. The maximum correction made at any state in the present experimental work was 2.4 per cent.

With all the correction terms taken into account the thermal conductivity of the fluid may be evaluated from the indication of a particular thermocouple by the following expression:

$$k = \left[\frac{(\underline{q}_m/d\theta)}{\Delta t_m}\right]\left[\frac{(r_o - r_i)}{4\pi r_o r_i}\phi_A K_p\right]\left[\frac{1}{1 - \frac{1}{\beta}\frac{(\underline{q}_m/d\theta)}{\Delta t_m}}\right] - k_r \qquad (3)$$

In the experimental program, measurements were usually made at four rates of energy addition for each state investigated. The value of the term $(\underline{q}_m/d\theta)/\Delta t_m$ at zero rate of energy addition was established by fitting a straight line through the data as a function of the energy rate by least squares methods. Values of the thermal conductivity were calculated from the extrapolated values at zero energy rate by use of equation (*3*). The reported values were taken as an area-weighted average of the results from the six thermocouples. This procedure established the thermal conductivity at the temperature of the agitated oil bath. The reported pressure is that measured when the entire cell was at the temperature of the bath.

The presence of convection was detected by a rapid increase of the term $(\underline{q}_m/d\theta)/\Delta t_m$ as the energy rate was increased. Convection was found only in the vicinity of the critical state at the energy rates used in this study.

The thermocouple voltages were measured on a potentiometer with a minimum dial reading of 0.01 microvolt. The thermocouples were calibrated by comparing their voltages, measured relative to an ice bath, with temperatures of the oil bath, established with a strain-free platinum resistance thermometer (*11*) when the cell was in equilibrium with the oil bath. The thermometer was calibrated by the National Bureau of Standards.

The spacing between spheres and the thermal resistance associated with the mountings of the individual thermocouples were determined by calibrating the cell with helium and argon as fluids. The values of thermal conductivity for argon were taken from Hilsenrath (*4*), and those for helium were taken from Keyes (*8*) and Hilsenrath (*3*). Both quantities were determined as a function of temperature at atmospheric pressure. The dimensions as determined by calibration with argon and helium agreed with values from direct measurement to within 0.001 in., which is within the accuracy of the methods of direct measurement. Presence of the gold plate made precision dimensional measurements unreliable.

Both methods of measurement indicated the spheres were concentric within 0.001 in., a difference which would make a negligible error in the measured thermal conductivity. The spacing determined by the measurements on helium and argon in the lower hemisphere was 2 per cent greater then that in the upper hemisphere.

The fraction of the temperature difference occurring between the surface of the sphere or the shell and the thermocouple junctions varied between the several thermocouples, which accounts for the thermal resistance term, $1/\beta$, assuming a different value for each thermocouple. The value of this fraction varied between 1 and 13 per cent depending on the state at which measurements were being made.

Agreement between the results based upon the different thermocouples was within 2 per cent, except at the highest pressures when a consistent difference up to 6 per cent was found between results based on the upper hemisphere and those for the lower hemisphere. This was caused by deformation of the outer shell, resulting in a relative displacement of the shell and the sphere. In all cases the results from the upper and lower hemispheres were averaged on a spatial basis to yield the final results. An analysis of the distortion indicated that the averaging method used was a valid procedure.

MATERIAL

The nitrous oxide was purchased from the Ohio Chemical Pacific Company, and was reported to contain less than 0.02 mole fraction impurities. It was subjected to several partial condensations at liquid nitrogen temperature, then passed in the gaseous state over activated alumina so that materials of higher molecular weight than nitrous oxide were adsorbed. The purified material exhibited a negligible change in vapor pressure with change in quality at 100° F.

EXPERIMENTAL RESULTS

Table I presents values of the thermal conductivity obtained in this investigation as well as the conditions associated with the measurements.

Table I. Experimental Measurements of Thermal Conductivity

Nominal Temperature ° F.	Pressure P.S.I.A.	Thermal Conductivity B.t.u./(Hr.)(Ft.)(° F.)
40	16.5	0.00899
	457	0.01137
	537	0.05845
	2175	0.06518
	4910	0.07427
100	20.8	0.01034
	631	0.01292
	1845	0.04607
	3188	0.05402
	4527	0.05754
220	20.8	0.01343
	1297	0.01755
	2949	0.03004
	4969	0.04123
340	20.8	0.01656
	1559	0.01963
	3191	0.02581
	5094	0.03313

The effect of the thermal flux between the spherical surfaces upon the quantity $(\underline{q}_m/d\theta)/\Delta t_m$ and upon the apparent thermal conductivity is shown in Figure 1. The "apparent thermal conductivity" is defined as that value calculated from the measurements at a particular flux, by the use of equation (3). The average temperature gradient in the fluid is indicated in the upper part of Figure 1. It is evident that differences existed in the thermal resistances of the thermocouple mountings, as shown by the different values of $(\underline{q}_m/d\theta)/\Delta t_m$ for the several thermocouples in the upper half of the figure. The results from all thermocouples were brought into agreement through use of the individual values of the thermal resistance, $1/\beta$, as seen in the lower half of Figure 1. Information similar to that in the figure was obtained for all the states investigated. The extrapolated values at zero thermal flux were used to calculate the thermal conductivity.

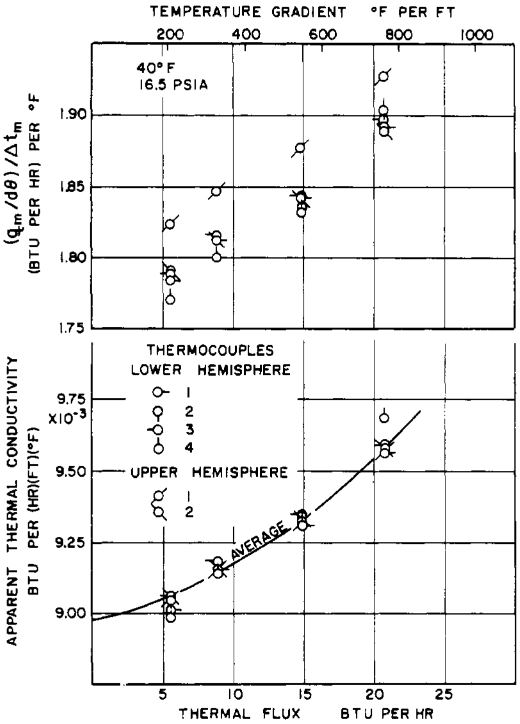

Figure 1. Effect of thermal flux upon apparent thermal conductivity

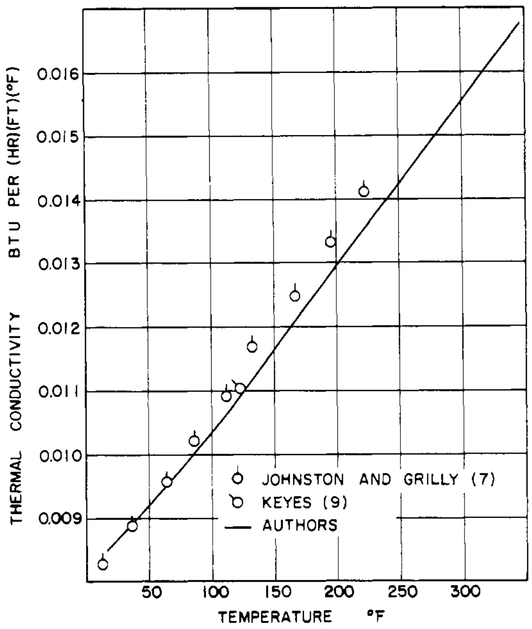

Figure 2. Thermal conductivity of nitrous oxide at atmospheric pressure

The influence of temperature upon the thermal conductivity of nitrous oxide at atmospheric pressure is shown in Figure 2 as well as the values of Johnston and Grilly (7) and a single measurement by Keyes (9). The present data indicate somewhat lower thermal conductivities at the higher temperatures than reported by Johnston and Grilly, but are in good agreement with Keyes.

Figure 3 portrays the influence of pressure upon the thermal conductivity of nitrous oxide for a series of temperatures. The data of Keyes at 122° F. are presented in Figure 4. An interpolated curve for 122° F. based upon the present data is included to illustrate the agreement between the measurements of Keyes and the present data. The standard error of estimate of Keyes' measurements from the smooth interpolated curve based on the present measurements is 0.0003 B.t.u./(hr.)(ft.)(° F.).

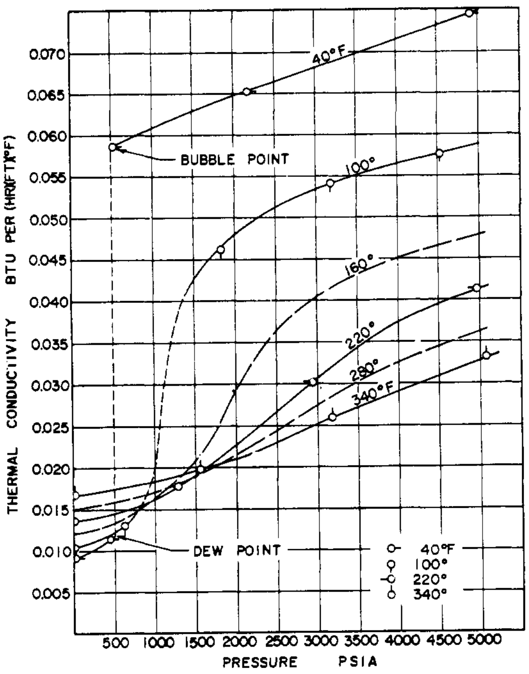

Figure 3. Influence of pressure upon thermal conductivity of nitrous oxide

Table II records smooth values of the thermal conductivity of nitrous oxide, as established from the measurements in Table I. The standard error of estimate of the present experimental data of Table I from the smooth data is 0.0002 B.t.u./(hr.)(ft.)(° F.).

Consideration of the accuracy of measurement of the dimensions of the equipment, of the rate of electrical energy addition to the inner sphere, and of the temperature differences indicated that, at a distance from the critical state the thermal conductivity was established with a probable uncertainty of 2 per cent. Near the critical state the onset of natural convection was of such intensity as to introduce greater uncertainty in the extrapolation of the apparent thermal conductivity to zero flux. Smooth values obtained from data affected by this condition are indicated in Table II.

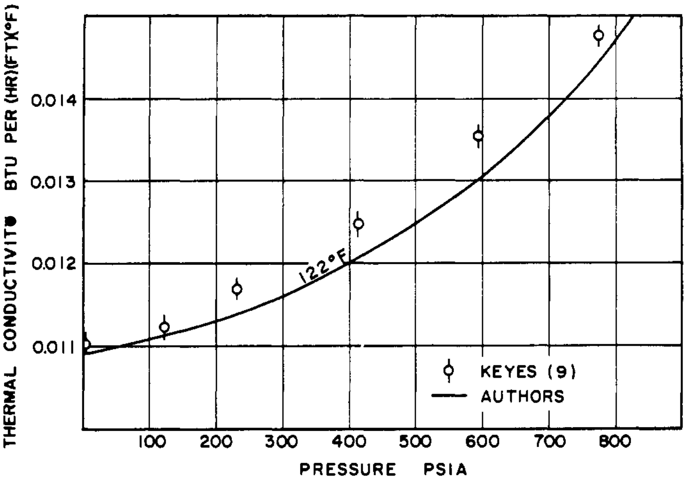

Figure 4. Comparison of measurements of thermal conductivity

The influence of the specific weight of nitrous oxide upon the residual thermal conductivity is shown in Figure 5. The "residual thermal conductivity" is defined as the difference between thermal conductivity at a given pressure and at attenuation for the same temperature. Specific weight at each state was taken from the recent data of Couch and Kobe (*1*) and of Hirth and Kobe (*5*). All the experimental measurements recorded in Table I have been included on this diagram as well as the data of Keyes(*9*). The standard error of estimate of the present experimental data from the smooth curve drawn in Figure 5 is 0.0002 B.t.u./(hr.)(ft.)(° F.), which corresponds to a deviation of approximately 0.46 per cent relative to the average thermal conductivity of nitrous oxide. Within the accuracy of the experimental measurements of thermal conductivity and specific weight of nitrous oxide, it appears that the residual thermal conductivity may be considered a single-valued function of specific weight of this compound. Experimental measurements of thermal conductivity in the immediate vicinity of the critical state were not sufficient to establish whether the relationship shown in Figure 5 is applicable to the same degree of accuracy for the vicinity of the critical point as for the conditions remote from this state.

Table II. Thermal Conductivity of Nitrous Oxide

Pressure P.S.I.A.	Temperature, ° F. 40	100	160[a]	220	280[a]	340
	(514)[b]					
Dew Point	0.0118					
Bubble Point	0.0585					
14.7	0.00900[c]	0.01034	0.01191	0.01348	0.01503	0.01658
200	0.00971	0.01078	0.01224	0.01370	0.01519	0.01676
400	0.01093	0.01159	0.01270	0.01408	0.01558	0.01708
600	0.05890	0.01261	0.01365	0.01469	0.01601	0.01744
800	0.05988	0.01436[d]	0.01492	0.01540	0.01648	0.01783
1000	0.06078	0.01935[d]	0.01636	0.01605	0.01697	0.01824
1000	0.06280	0.04250[d]	0.02061	0.01880	0.01879	0.01948
2000	0.06465	0.04792	0.02901	0.02249	0.02139	0.02099
2500	0.06637	0.05113	0.03615	0.02651	0.02420	0.02293
3000	0.06802	0.05331	0.04023	0.03050	0.02726	0.02507
3500	0.06965	0.05494	0.04299	0.03426	0.03008	0.02707
4000	0.07128	0.05638	0.04495	0.03725	0.03242	0.02896
4500	0.07289	0.05753	0.04639	0.03925	0.03449	0.03078
5000	0.07458	0.05881	0.04760	0.04118	0.03611	0.03260

[a] Values of thermal conductivity at this temperature are interpolated. [b] Vapor pressure expressed in P.S.I.A. [c] Thermal conductivity expressed in B.t.u./(hr.)(ft.)(° F.). [d] Estimated.

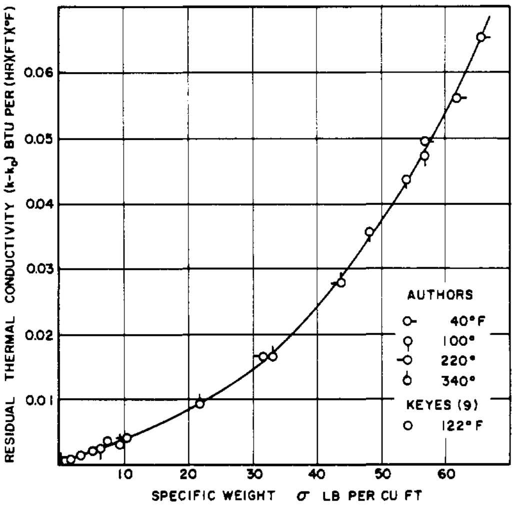

Figure 5. Variation in residual thermal conductivity with specific weight

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NOMENCLATURE

d = differential operator
K_p = correction factor for change of dimensions with pressure
k = thermal conductivity, B.t.u./(hr.)(ft.)(° F.)
k_o = thermal conductivity at attenuation
k_r = coefficient of thermal transport by radiation, B.t.u./(hr.)(ft.)(° F.)
k_s = coefficient of thermal transport through stem, B.t.u./(hr.)(ft.)(° F.)
$q_m/d\theta$ = measured rate of energy addition, B.t.u./hr.
r_i = inner radius, ft.
r_o = outer radius, ft.
t_i = temperature at inner radius, ° F.
t_o = temperature at outer radius, ° F.
Δt_m = measured temperature difference, ° F.
β = reciprocal thermal resistance associated with a thermocouple mounting B.t.u./(hr.)(ft.)
θ = time, hr.
σ = specific weight, lb./cu. ft.
ϕ_A = ratio of area of complete sphere to that of sphere minus area intercepted by shaft

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