Thermal Conductivity of Fluids. Ammonia

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The thermal conductivity of ammonia was measured in a spherical conductivity cell at pressures up to 5000 p.s.i.a. in the temperature interval between 40° and 400° F. The results at atmospheric pressure agree satisfactorily with earlier measurements. The residual thermal conductivity was a single-valued function of specific weight for both the liquid and gas phases. The investigation did not include the critical region.

ALTHOUGH AMMONIA is an important industrial material, there have been only limited investigations of its thermal conductivity at elevated pressures. At or near atmospheric pressure, the measurements of Callear and Robb (*2*), Dickins (*4*), Eucken (*5*), Franck (*6*), Gray and Wright (*7*), and the review in the International Critical Tables (*9*) are available. Keyes (*10*) also carried out measurements at atmospheric pressure and extended his work at a single temperature to a maximum pressure of about 135 p.s.i.a. Recently, Ziebland and Needham (*13*) reported graphically some preliminary values at elevated pressures. As a result of the paucity of experimental data concerning the thermal conductivity of ammonia at elevated pressures, a limited study of this property at pressures up to 5000 p.s.i.a. is reported here in the temperature interval between 40° and 400° F. A comparison with the earlier data has been included.

Methods. The details of the equipment used in this investigation have been described (*11*). In principle, it consisted of a sphere within which was located an electrical heater and thermocouples near the external surface. This sphere, approximately 3.5 inches in diameter, was surrounded by a spherical pressure vessel provided with thermocouples near its inner surface. The inner surface of the pressure vessel and the outer surface of the inner sphere were gold plated and polished.

The entire apparatus was immersed in an agitated silicone bath whose temperature did not vary with respect to either time or position by more than 0.005° F. Measurements of the temperature differences across the spherical gap of approximately 0.020 inch were made as a function of the electrical energy addition to the inner sphere. The apparent thermal conductivity was calculated as a function of flux for each of the several thermocouples. Appropriate corrections were made for the minor variations in the positions of the thermocouples with respect to the adjacent surface and for the temperature gradient in the stainless steel used in making the inner sphere and the outer pressure vessel (*11*). The methods and calculations have also been described in a previous manuscript (*11*).

Thermal fluxes employed in this investigation varied between 1.6454 and 46.5747 B.t.u./(hr.)(sq. ft.). Corresponding temperature differences varied between 0.273° and 2.460° F. Measurements of the thermal conductivity of helium near atmospheric pressure were carried out at periodic intervals during this investigation. The results obtained agreed with the critically chosen value reported by Hilsenrath and Touloukian (*8*). It is believed that the values of the thermal conductivity herein reported did not involve uncertainties larger than 3%. Such a large uncertainty resulted in part from the measurements made early in the life of the thermal conductivity equipment when variation in calibration with respect to time was experienced.

Material. The ammonia used for this investigation was obtained from the Barrett Division of Allied Chemical and Dye Corp. The measured vapor pressure of this material agreed with reported values (*12*). It is believed that the material was of sufficient purity not to introduce any measurable uncertainty in the results.

EXPERIMENTAL RESULTS

The lower part of Figure 1 shows the effect of thermal flux upon the apparent thermal conductivity for ammonia at 618 p.s.i.a. and at a temperature of 160° F. The increase in apparent thermal conductivity with thermal flux resulted in part from an increase in the average temperature of measurement and from local convection at the higher values of thermal flux. In the upper part of Figure 1 the quotient of the thermal flux and the temperature difference is depicted. The effect of location of the thermocouples upon these uncorrected data is evident. At a few of the states where measurements were attempted, the natural convection persisted throughout the transport path and resulted in a marked increase in thermal conductivity with thermal flux. Results obtained under these circumstances were not included in this investigation.

The spread of the values extrapolated to zero thermal flux shown in the example depicted in Figure 1 results in part from difficulty in taking into account properly the effect of thermal flux and position on the indications of the thermocouples. The methods employed in making such corrections have been described (*11*). In addition, a linear relationship between the apparent thermal conductivity and the thermal flux was assumed in this range of flux. Undoubtedly, this was not strictly true. A significant part of the indicated variation of apparent thermal conductivity

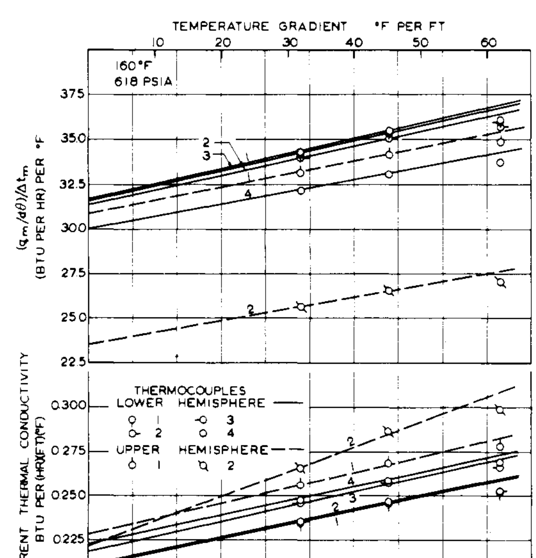

Figure 1. Effect of thermal flux upon apparent thermal conductivity

with thermal flux resulted from a change in the average temperature of the fluid in the transport path. In the opinion of the authors, the assumption of a linear relationship between the apparent thermal conductivity and flux and the fitting of these lines to the experimental data was preferable to attempting a more elaborate description of the probable physical situation. The standard deviation of the apparent thermal conductivity extrapolated to zero thermal flux for each thermocouple was 3.3% when averaged for all the points taken.

In measurements of this type, the onset of gross natural convection limits the temperature gradients which can be employed. With the present equipment, there was a gradual increase in apparent thermal conductivity with flux, as shown in Figure 1. This gradual increase was followed by an abrupt and rapid increase of apparent thermal conductivity with flux at higher values of the thermal flux than are shown in Figure 1. The onset of gross natural convection of this type can be predicted roughly from the conventional linear criteria. However, in the case of a spherical cell there is some opportunity for local instability, particularly near the upper pole.

It is difficult to predict from linear considerations the initiation of such local instabilities. Their existence may well contribute to the influence of thermal flux upon the apparent thermal conductivity at the lowest fluxes and associated temperature gradients where accurate measurements of the latter quantity could be made. Behavior of the latter type is shown in Figure 1. At higher thermal fluxes there is an abrupt and marked increase in the rate of change of apparent thermal conductivity with flux. Such behavior indicates the onset of natural convection, particularly around the equator of the thermal conductivity cell.

With an increase in pressure there was a slight displacement from concentricity of the inner sphere with respect to the outer cavity. This displacement amounted to approximately 0.001 inch at the maximum pressures studied. An analysis of the situation indicates that for such orders of displacement a linear average of the behavior in the lower and upper hemispheres was satisfactory. This displacement probably accounts for the larger standard deviations shown in Table I for the higher pressures. The change in the radial dimension of the gap was taken care of on the basis of conventional elastic theory. A more detailed discussion of this situation is available (*11*).

The uncertainties of the experimental results have been expressed in terms of the standard deviation or standard error of estimate normally associated with a linear regression analysis. The choice of a measure of uncertainty is arbitrary and the standard deviation or the standard error of estimate has been employed as is appropriate, because of the familiarity of these terms in the technical literature.

In Table I are recorded the experimental measurements for the thermal conductivity of ammonia. The results represent the area-weighted average values of the extrapolation to zero flux of the individual thermocouple measurements of the apparent thermal conductivity. The extrapolation was shown in Figure 1. The standard deviation of the individual measurements from the area-weighted average at zero flux has been included in Table I.

Figure 2 depicts the experimental values of the thermal conductivity of ammonia at zero thermal flux as a function of pressure for each of the several temperatures investigated. The standard error of estimate of these values of thermal conductivity from the smooth data was 0.0016 B.t.u./(hr.)(ft.)(° F.). The behavior at 280° F., which was similar to that encountered with other fluids in the critical region, has been indicated by a dashed curve, since insufficient measurements were obtained to establish the behavior in this region with an accuracy equivalent to that at other states more remote from the critical region. The behavior in the gaseous region is shown in an insert in the upper part of the figure.

The thermal conductivity of ammonia at atmospheric pressure is shown as a function of temperature in Figure 3. The smooth curve represents values taken from Figure 2. The literature values (*2, 4–7, 9, 10*) have been included for comparison. The standard error of estimate of the measurements of Keyes from the current data was 0.0006 B.t.u./(hr.)(ft.)(° F.), and the data of Franck yielded a standard error of estimate of 0.0014 B.t.u./(hr.)(ft.)(° F.). The experimental values of Gray and Wright yielded a

Table I. Experimental Results

Press., P.S.I.A.	Thermal Conductivity, B.t.u./(Hr.)(ft.)(° F.)	Std. Dev.[a], B.t.u./(Hr.)(ft.)(° F.)
	40° F.	
17	0.01248	0.00016
36	0.01292	0.00012
132	0.2941	0.01129
1150	0.2992	0.01153
2055	0.3007	0.01070
	100° F.	
16	0.01437	0.00048
38	0.01525	0.00072
167	0.01854	0.00022
329	0.2613	0.01042
2525	0.2689	0.01224
4988	0.2919	0.02102
	160° F.	
15	0.01783	0.00019
212	0.01953	0.00047
415	0.02249	0.00024
618	0.2204	0.00569
2116	0.2298	0.00921
3796	0.2471	0.01545
	220° F.	
15	0.01948	0.00078
240	0.02207	0.00022
485	0.02322	0.00026
904	0.03204	0.00024
1055	0.1541	0.00306
2973	0.1924	0.00801
4952	0.2265	0.01613
	280° F.	
17	0.02307	0.00016
212	0.02390	0.00022
548	0.02737	0.00036
1182	0.03303	0.00024
	340° F.	
19	0.02428	0.00029
229	0.02609	0.00021
1685	0.03963	0.00068
3427	0.11167	0.00355
5299	0.1493	0.00783
	400° F	
15	0.02799	0.00064
247	0.02873	0.00027
1958	0.03963	0.00058
3407	0.07291	0.00177
4951	0.10385	0.00419

[a] Standard deviation from the area-weighted average of the six thermocouples as calculated from: $S = \left[\left\{\sum_{1}^{N} (k_m - k)^2\right\}/N\right]^{1/2}$

value of the standard error of estimate of 0.0009 B.t.u./(hr.)(ft.)(° F.). The present values were slightly higher at the intermediate temperatures than those reported by the other investigators.

Abas-Zade (*1*) proposed that the residual thermal conductivity, defined as the difference between thermal conductivity at a given pressure and the value at attenuation for the same temperature, should be a single-valued function of specific weight. In considering the behavior of the fluid at low pressures, the term "attenuation" has been employed to describe the state at low pressures where the mean free path of the molecules was still small as compared with the radial dimensions of the space between the concentric spherical surfaces. The information reported by the Bureau of Standards Circular (*12*) was used to establish the specific weight of ammonia as a function of pressure and temperature.

Figure 4 shows the residual thermal conductivity as a function of the specific weight of ammonia. The experimental results of the current investigation are set forth in this figure. The standard error of estimate of these measurements from the smooth curve drawn through these data was 0.0047 B.t.u./(hr.)(ft.)(° F.). The deviation of the present data from this single-valued function is greater than that found by the authors for nitrous oxide (*11*) or for ethane (*3*).

As a matter of interest, the experimental measurements of Keyes (*10*) are given in an insert to Figure 5 on a residual basis. In the relatively small range of specific weights involved, these measurements yield a standard error of estimate of 0.0002 B.t.u./(hr.)(ft.)(° F.) from the present measurements. The values obtained by the authors from the graphical presentation of Ziebland and Needham (*13*) have also been included in Figure 5. These data yield a standard error of estimate of 0.0066 B.t.u./(hr.)(ft.)(° F.).

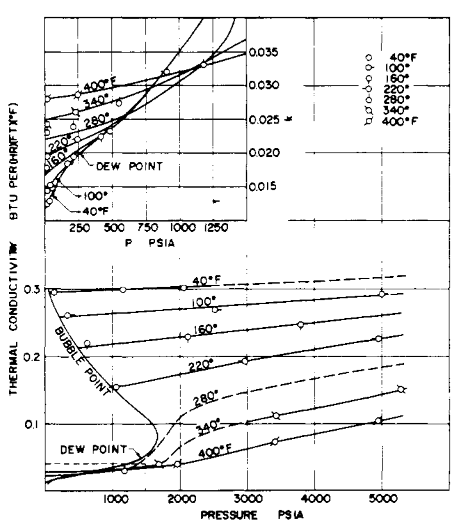

Figure 2. Effect of pressure upon thermal conductivity

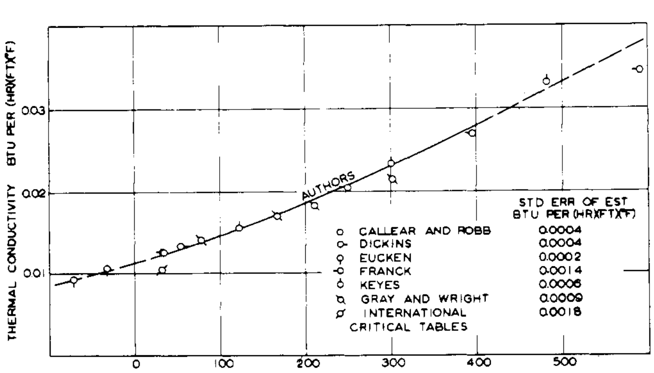

Figure 3. Thermal conductivity at atmospheric pressure

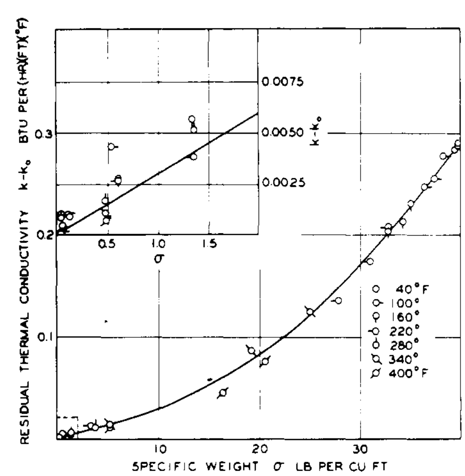

Figure 4. Residual thermal conductivity for ammonia

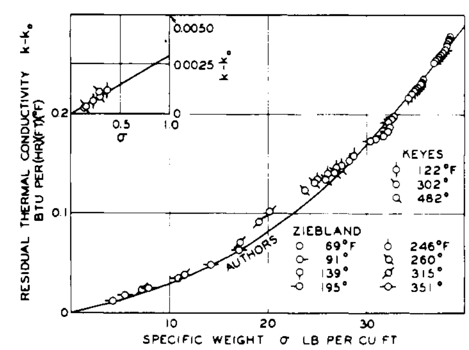

Figure 5. Comparison with measurements of other investigators

Table II records smooth values of the thermal conductivity of ammonia as a function of pressure and temperature. The data correspond to the information presented by the smooth curves in Figure 2, where the standard error of estimate was 0.0016 B.t.u./(hr.)(ft.)(° F.). Table II also includes the standard error of estimate of the smooth values from the experimental measurements recorded in Table I. Upon review of these data and comparison with the limited experimental work available, it is probable that the results in Table II involved an experimental uncertainty of approximately 2.5%.

It is quite possible that at states near the critical state of ammonia, the residual thermal conductivity may deviate from the full curve shown in Figure 5. Ziebland's data (*13*) are indicative of such behavior. For this reason the information submitted in Figure 4 and in Table II should not be employed to estimate the thermal conductivity in the critical region.

ACKNOWLEDGMENT

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Table II. Thermal Conductivity of Ammonia

Press., P.S.I.A.	Temperature, ° F. 40	100	160	220	280	340	400
Dew Point	0.0149	0.0192	0.0236	0.0347			
Bubble Point	0.294	0.258	0.212	0.153			
14.7	0.0125[a]	0.0146	0.0170	0.0195	0.0222	0.0250	0.0280
200	0.294	0.0190	0.0199	0.0214	0.0231	0.0259	0.0285
400	0.295	0.259	0.0224	0.0228	0.0242	0.0269	0.0293
600	0.296	0.260	0.214	0.0257	0.0257	0.0283	0.0301
800	0.297	0.261	0.216	0.0301	0.0280	0.0298	0.0310
1000	0.298	0.263	0.218	0.153	...[b]	0.0315	0.0320
1500	0.300	0.266	0.223	0.163	...	0.0368	0.0348
2000	0.302	0.269	0.228	0.172	...	0.0660	0.0400
2500	0.304	0.272	0.234	0.183	...	0.0900	0.0503
3000	0.306	0.276	0.239	0.193	0.147	0.1034	0.0629
3500	0.308	0.279	0.244	0.202	0.157	0.1134	0.0750
4000	0.310	0.282	0.250	0.211	0.167	0.123	0.0855
4500	0.313	0.286	0.255	0.219	0.176	0.133	0.0954
5000	0.316	0.289	0.260	0.227	0.184	0.143	0.104
σ[c]	0.0007 (73)[d]	0.0024 (212)[d]	0.0027 (492)[d]	0.0004 (989)[d]	0.0013	0.0003	0.0004

[a] Thermal conductivity expressed in B.t.u./(hr.)(ft.)(° F.). [b] Experimental data were not obtained in the critical region. [c] Standard error of estimate σ expressed in B.t.u./(hr.)(ft.)(° F.). [d] Vapor pressure of ammonia expressed in pounds per square inch *(12)*.

$$\sigma = \left[\left\{ \sum_1^N (k_e - k_s)^2 \right\} / N \right]^{1/2}$$

NOMENCLATURE

k = thermal conductivity, B.t.u./(hr.)(ft.)(° F.)
k_o = thermal conductivity at attenuation, B.t.u./(hr.)(ft.)(° F.)
N = total number of experimental points
$q_m/d\theta$ = measured rate of energy addition, B.t.u./hr.
Δt_m = measured temperature difference, ° F.
θ = time, hr.
σ = specific weight, lb./cu. ft.
σ = standard error of estimate

Subscripts

e = experimental
m = area-weighted average
s = smooth

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