The Thermal Conductivity of Nonpolar Substances in the Dense Gaseous and Liquid Regions

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In 1949 Gamson (*13*) produced a reduced state correlation from available thermal conductivity data in which the reduced thermal conductivity, k/k_c, is plotted against reduced temperature and pressure. Experimental data, which were subsequently obtained, were found to deviate considerably from values resulting from Gamson's correlation (*45*). Comings and Nathan (*9*) combined the Enskog relationships for viscosity and thermal conductivity to obtain an expression for the ratio, k/k^*, in terms of the viscosity ratio, μ/μ^*, and the quantity, y. In the resulting relationship, the effects of the internal degrees of freedom of the molecules are neglected. Values of y were obtained from experimental P-V-T data as suggested by Enskog (*10*), and experimental and calculated viscosities were used to develop a correlation between k/k^* and reduced temperature and pressure.

Lenoir and Comings (*29*) found that their experimental thermal conductivities for argon, nitrogen, methane, ethylene, and carbon dioxide were in good agreement with those resulting from the correlation of Comings and Nathan. Lenoir, Junk, and Comings (*30*) used their experimental values for nitrogen, methane, and argon, and the values obtained previously by Lenoir and Comings to develop a new correlation for k/k^* which is very similar to that of Comings and Nathan, except that it predicts higher values for conditions in the vicinity of the critical point. Thermal-conductivity values determined by Lenoir, Junk, and Comings for ethane were found to be inconsistent with corresponding values resulting from their correlation, as were the subsequent values obtained by Leng and Comings (*28*) for propane and those of Kramer and Comings (*27*) for n-butane. Therefore, it would be desirable to develop an improved correlation for thermal conductivity which is also applicable to a wider range of substances.

Jossi, Stiel, and Thodos (*20*) have obtained reliable expressions for the viscosity of pure substances in the dense gaseous and liquid phases by the use of a relationship between the residual viscosity, $\mu - \mu^*$, and density, along with a dimensional analysis approach. Thodos and coworkers (*22, 38, 47, 48*) have found that the residual thermal conductivity, $k - k^*$, is a unique function of density for all the substances investigated. A theoretical basis for such a dependence has been provided by Predvoditelev (*41*). Therefore, in the present study an approach similar to that of Jossi, Stiel, and Thodos for viscosity has been utilized to develop a generalized correlation for the thermal conductivity of nonpolar substances by the use of the residual relationship for this property and dimensional analysis.

DIMENSIONAL ANALYSIS

Several investigators have suggested that the thermal conductivity in the dense gaseous and liquid regions is dependent on C_p, the heat capacity (*10, 12*). If this variable is included in a dimensional analysis treatment of the residual relationship, the resulting expression would indicate that the residual thermal conductivity is dependent on variables other than the density. However, such a dependence is inconsistent with the conclusions of the previous investigators that $k - k^*$ is dependent only on the density and dimenional constants specific to each substance. If as in the previous treatment for viscosity (*20*) these variables are assumed to be the molecular weight and critical constants of the substance, the application of the Rayleigh method of dimensional analysis leads to the following development:

$$k - k^* = \alpha T_c{}^a P_c{}^b v_c{}^c R^d M^e v^f \tag{1}$$

The dimensions involved are mass, length, time, and temperature. The following values for the exponents result:

$$a = d - 1 \qquad d = d$$

$$b = \frac{3}{2} - d \qquad e = -\frac{1}{2}$$

$$c = \frac{5}{6} - d - f \qquad f = f$$

By the use of these exponents, Equation (1) becomes

$$(k - k^*)\lambda = \beta\, z_c{}^m\, \rho_R^{\,n} \tag{2}$$

where $\beta = \alpha R^{5/6}$ (α is a dimensionless constant), $m = \frac{5}{6} - d$, $n = -f$, $\rho_R = \frac{v_c}{v}$, and $\lambda = T_c{}^{1/6}M^{1/2}/P_c{}^{2/3}$.

TREATMENT OF EXPERIMENTAL THERMAL-CONDUCTIVITY DATA

Experimental data available in the literature for 20 nonpolar substances, including the inert gases, diatomic gases, carbon dioxide, aliphatic hydrocarbons, and aromatics were used to establish the coefficient, β, and exponents, m and n, of Equation (2). The substances are listed in Table 1 along with their molecular weights, critical constants, calculated values of λ, and the sources of the thermal conductivity and density data used.

From the reported high pressure and atmospheric thermal conductivities, values of $(k - k^*)\lambda$ were calculated for each substance and plotted on log-log coordinates against the corresponding reduced density. Essentially identical relationships resulted for substances with similar critical compressibility factors. Although for the viscosity of nonpolar substances (*20*)

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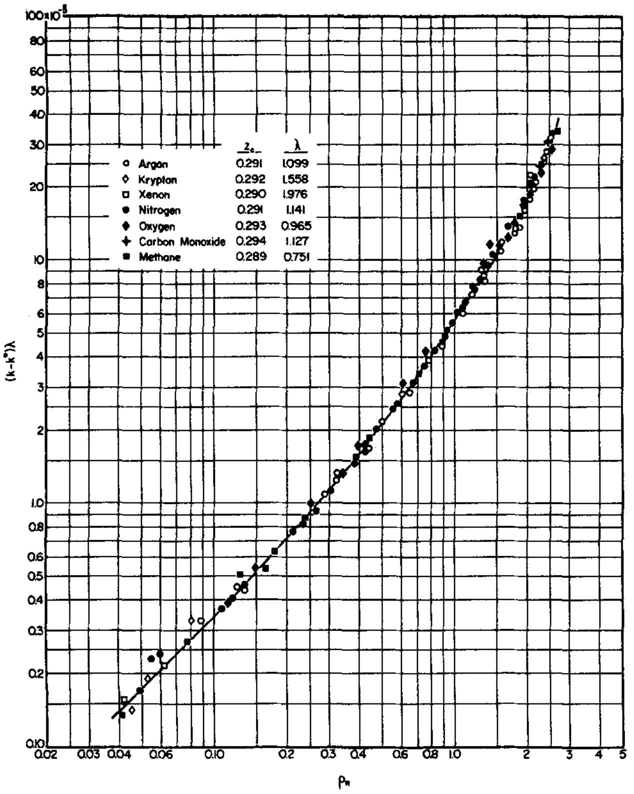

Fig. 1. Relationship between $(k\text{-}k^*)\ \lambda$ and ρ_R for substances having $z_C \approx 0.291$.

relationships between $(\mu - \mu^*)\xi$ and ρ_R were found to be independent of z_c, $(k - k^*)\lambda$ is highly dependent on this variable.

In Figure 1 a composite curve relating $(k - k^*)\lambda$ to ρ_R is presented for substances whose critical compressibility factors are approximately $z_c = 0.291$, including argon, krypton, xenon, nitrogen, oxygen, carbon monoxide, and methane. It can be seen from this figure that nearly all of the data for the seven substances are in good agreement and that the exponent n in Equation (2) is not a constant, but instead the dependence of $(k - k^*)\lambda$ on ρ_R is a complex continuous function. The data of Michels, Botzen, Friedman, and Sengers (*34*) for argon and those of Michels and Botzen (*33*) for nitrogen were found to be inconsistent with the values presented in Figure 1. These investigators used a parallel-plate method for determining thermal conductivities which is effective for the elimination of convection but possesses the disadvantage of end effects, which are very difficult to take into account (*14*). The data of Uhlir (*58*), Ziebland (*62*), and Keyes (*23, 24, 25*) for argon and nitrogen and of Johannin (*19*) for nitrogen were in close agreement and were therefore accepted for these substances. Johannin (*19*) used the coaxial-cylinder method for the determination of thermal conductivities and made very careful measurements of the thermal conductivity of nitrogen for temperatures up to 700°C. and pressures up to 1,600 atm. The conditions of his study are considerably removed from the critical point where accurate measurements are difficult to obtain because of convective effects. The data of Johannin (*19*) produce a smooth relationship between $(k - k^*)\lambda$ and ρ_R and serve to confirm that the residual relationship is applicable over a wide range of temperatures and pressures. Although Johannin has reported that residual thermal conductivities resulting from his data are dependent on both temperature and density (*19*), deviations of more than 2% of this type could not be detected in the present study. These conflicting conclusions may be due to the fact that density data used by Johannin differed from those used in the present study.

The relationships between $(k - k^*)\lambda$ and ρ_R were essentially parallel for all the substances investigated. Therefore, values of $(k - k^*)\lambda$ were read for each substance at constant reduced densities and were plotted against the corresponding critical compressibility factor on log-log coordinates. In this manner, the exponent m of z_c in Equation (2) was established to be approximately 5.0. In Figure 2 a composite curve relating $(k - k^*)\lambda z_c^5$ to ρ_R is presented for all the twenty substances investigated. The following values were read for an enlarged plot of Figure 2 and can be used to calculate the thermal conductivity of nonpolar substances in the dense gaseous and liquid regions:

ρ_R	$(k - k^*)\lambda$ $z_c^5 \times 10^8$	ρ_R	$(k - k^*)\lambda$ $z_c^5 \times 10^8$
0.04	0.30	0.60	5.58
0.06	0.44	0.80	8.40
0.08	0.57	1.00	11.6
0.10	0.72	1.20	15.2

TABLE 1. BASIC CONSTANTS AND SOURCES OF DATA

	M	T_c, °K.	P_c, atm.	ρ_c, g./cc.	z_c	λ	Sources of thermal-conductivity data (dense gaseous and liquid phases)	Sources of density values (dense gaseous and liquid phases)
Argon	39.94	150.9	48.34	0.536	0.291	1.099	24, 25, 29, 30, 34, 58, 62	16
Krypton	83.70	209.4	58.18	0.908	0.292	1.558	25	16
Xenon	131.30	289.8	57.64	1.099	0.290	1.976	25	16
Nitrogen	28.02	126.2	33.5	0.311	0.291	1.141	2, 3, 5, 15, 19, 23, 25, 26, 29, 30, 33, 40, 54, 55, 58, 59, 62	8
Oxygen	32.00	154.8	50.1	0.430	0.293	0.965	2, 15, 25, 42, 57, 61	8
Carbon monoxide	28.01	133	34.5	0.301	0.294	1.127	5	8
Carbon dioxide	44.01	304.2	72.85	0.467	0.275	0.987	4, 14, 23, 29, 49, 55	21
Methane	16.04	191.1	45.8	0.162	0.289	0.751	5, 24, 25, 29, 30	32
Ethylene	28.05	282.4	50.0	0.227	0.267	0.989	2, 5, 24, 29	60
Ethane	30.07	305.4	48.20	0.203	0.285	1.072	24, 28, 30	39
Propane	44.09	370.0	42.0	0.220	0.277	1.469	28	44
n-Butane	58.12	425.4	37.43	0.228	0.273	1.800	27	36
n-Pentane	72.15	469.8	33.32	0.232	0.269	2.279	52	56
n-Hexane	86.17	507.9	29.9	0.234	0.264	2.717	51, 52	56
n-Heptane	100.20	540.2	27.0	0.235	0.260	3.165	3, 52	56
n-Octane	114.22	569.4	24.6	0.233	0.258	3.634	51, 52	56
n-Nonane	128.2	595.4	22.6	0.238	0.250	4.102	52	56
Cyclohexane	84.16	553.2	40.0	0.273	0.272	2.240	7, 46	56
Benzene	78.11	562.2	48.6	0.300	0.274	1.904	1, 7, 51	56
Toluene	92.13	594	41.6	0.290	0.271	2.312	1, 51	56

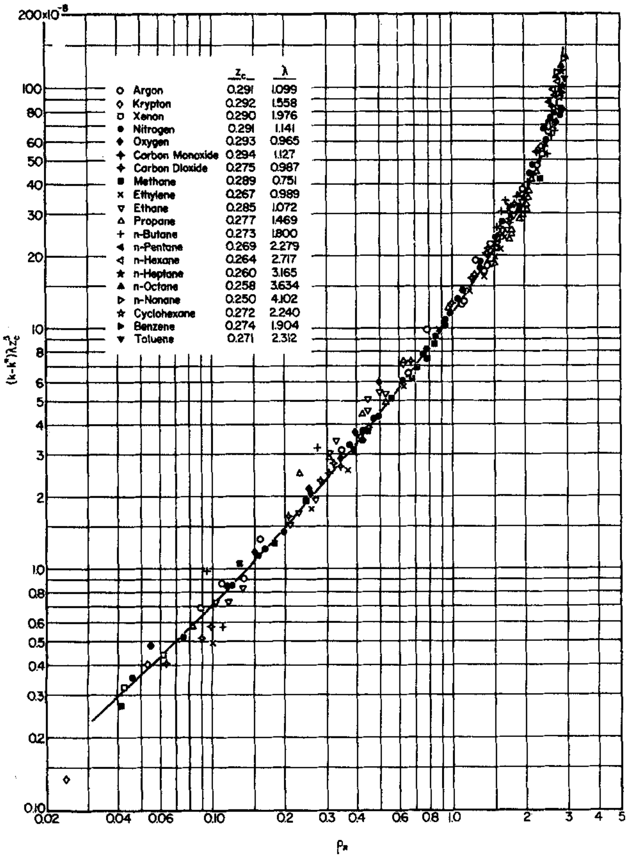

Fig. 2. Relationship between $(k\text{-}k^*)\lambda\ z^5{}_c$ and ρ_R for nonpolar substances.

0.125	0.90	1.40	19.5
0.150	1.08	1.60	24.0
0.175	1.28	1.80	29.5
0.200	1.48	2.00	36.0
0.25	1.90	2.20	43.8
0.30	2.37	2.40	53.0
0.40	3.32	2.60	66.0
		2.80	89.0

The following analytical representations of Figure 2 which permit the rapid calculation of thermal conductivity values were obtained:

$$(k - k^*)\,\lambda\, z_c{}^5 = 14.0\ [e^{-0.535\rho R} - 1] \times 10^{-8} \qquad \rho_R < 0.50 \qquad (3)$$

$$(k - k^*)\,\lambda\, z_c{}^5 = 13.10\ [e^{0.67\rho R} - 1.069] \times 10^{-8} \qquad 0.50 < \rho_R < 2.00 \qquad (4)$$

$$(k - k^*)\,\lambda\, z_c{}^5 = 2.976\ [e^{1.155\rho R} + 2.016] \times 10^{-8} \qquad 2.00 < \rho_R < 2.80 \qquad (5)$$

RESULTS AND CONCLUSIONS

The thermal-conductivity data for hydrogen and helium were found to be inconsistent with the relationship of Figure 2, probably because of the significant quantum effects exhibited by these substances, and were therefore not included. The relationships between $(k - k^*)\lambda$ and ρ_R for water and ammonia were found to follow roughly the same trend with z_c as the nonpolar substances, but were not parallel to the curve of Figure 2. Therefore water and ammonia could not be included in the correlation. An additional study is necessary to establish the thermal-conductivity behavior of polar substances in the dense gaseous and liquid regions.

Leng and Comings (*28*) and Kramer and Comings (*27*) found unexpected humps in the thermal-conductivity isotherms of propane and n-butane in the vicinity of the bubble point. They attributed this to the instability of the liquid phase in this region or to molecular rearrangement of the liquid. Sharp peaks were also obtained by these investigators in the vicinity of the critical point. These peaks were attributed to convection. Several investigators have attempted to measure accurately the thermal conductivity in the critical region by extrapolating the temperature gradient to zero (*14, 50*) in an attempt to eliminate convective effects. They concluded that the true thermal conductivity still undergoes a sharp increase in the critical region similar to the heat capacity.

In the present study, these effects have not been considered, and instead a smooth curve was drawn through the gaseous and liquid points which is continuous in the critical region. The thermal conductivity is difficult to measure in this region, since at the critical point the product of the Grashof and Prandtl numbers, which is a criterion for convection, becomes infinite. The data of Johannin, who avoided the critical region, produce a smooth relationship between $(k - k^*)\lambda$ and ρ_R which does not have a peak at $\rho_R = 1.00$. If the residual thermal conductivity is dependent only on density in the vicinity of $\rho_R = 1.00$, as it was found to be at higher or lower densities, it follows that the thermal conductivity should be continuous through the critical region. However, even if the thermal conductivity does exhibit a marked increase near the critical point, the relationship of Figure 2 should still be applicable over a wide range of temperatures and pressures.

In Figure 2, only those experimental points which are considered to be reliable are included, and the anomalous data for the critical region and for hydrocarbons are not presented in this figure. Because of the wide scatter of the experimental thermal-conductivity data, no meaningful comparison between experimental values and those resulting from the relationship of Figure 2 could be made without arbitrarily neglecting a certain amount of data. However, in most cases the agreement with experimental values is less than 10%, and for the data considered to be the most reliable (*19, 62*) the agreement was considerably better. A scatter of 6% in experimental values of the thermal conductivity at atmospheric pressures is not uncommon.

For liquids, since k^* is small compared with k, the relationship of Figure 2 indicates that the thermal conductivity of each substance investigated is dependent only on density. This dependence is consistent with the theoretical equation derived by Predvoditelev (*41*) for liquids

$$k = s\rho^{4/3} \qquad (6)$$

where s is a specific constant for each substance. However, at high densities the slope of the relationship of Figure 2 is approximately 2.25. Leng and Comings (*28*) report a slope of 2.2 for the relationship between k and ρ obtained from their liquid data for butane. The residual thermal conductivity is approximately proportional to $\rho^{4/3}$, as predicted by Predvoditelev, only below $\rho_R = 1.00$. From semitheoretical considerations, Bridgman (*6*) developed a relationship for the thermal conductivity of liquids, in terms of the velocity of sound in the liquid and the density, which can be combined with Rao's empirical expression for the velocity of sound (*43*) to produce the relationship

$$k = w\rho^{3.7} \qquad (7)$$

where w is a specific constant for each substance. Equation (7) predicts a larger dependence of thermal conductivity on density than that found in the present study.

THERMAL CONDUCTIVITY OF NONPOLAR GASES AT ATMOSPHERIC PRESSURE

In order to obtain thermal-conductivity values for nonpolar substances at high pressures from the relationship of Figure 2, the corresponding values of k^* at the same temperatures and atmospheric pressure must be available. Values of the thermal conductivity of monatomic gases at atmospheric pressure, k_m^*, can be calculated from the theoretical relationship of Hirschfelder, Curtiss, and Bird (*18*). Stiel and Thodos (*53*) have presented relationships for the prediction of the necessary force constants from the critical properties of the substance.

The theoretical relationship must be multiplied by a correction factor to account for the internal degrees of freedom of the molecules such as those proposed by Eucken (*11*) and Hirschfelder (*17*). Mason and Monchick (*31*) have recently developed a correction factor in which the thermal conductivity is dependent on the relaxation of the gas. Values of k calculated with the Mason and Monchick correction factor were found to be in very good agreement with the corresponding experimental values (*31, 37*). In this study the following expression was found to be a good approximation to the Mason-Monchick correction factor for most substances:

$$\frac{k_p^*}{k_m^*} = 0.307\frac{C_v}{R} + 0.539 \tag{8}$$

Therefore, Equation (8) can be used with the theoretical relationship for k_m^* to calculate the thermal conductivity of nonpolar substances at atmospheric pressure. For hydrocarbons the equations developed by Misic and Thodos (*35*) with a dimensional analysis approach can also be used.

NOTATION

a,b,c,d,e,f = exponents for Equation (1)
C_p = heat capacity at constant pressure, cal./g.-mole °K.
C_v = heat capacity at constant volume, cal./g.-mole °K.
k = thermal conductivity, cal./sec. cm. °K.
k^* = thermal conductivity at atmospheric pressure, cal./sec. cm. °K.
k_c = thermal conductivity at the critical point, cal./sec. cm. °K.
k_m^* = thermal conductivity of a monatomic gas at atmospheric pressure, cal./sec. cm. °K.
k_p^* = thermal conductivity of a polyatomic gas at atmospheric pressure, cal./sec. cm. °K.
m,n = exponents in Equation (2)
M = molecular weight
P = pressure, atm.
P_c = critical pressure, atm.
P_R = reduced pressure, P/P_c
R = gas constant, 1.987 cal./g.-mole °K.
s = constant in Equation (6)
T = temperature, °K.
T_c = critical temperature, °K.
T_R = reduced temperature, T/T_c
v = molar volume, cc./g.-mole
v_c = critical volume, cc./g.-mole
w = constant in Equation (7)
η = Enskog modulus, $\frac{v}{R}\left(\frac{\partial P}{\partial T}\right)_v - 1$
z_c = critical compressibility factor, $P_c v_c/RT_c$

Greek Letters

α = dimensionless constant in Equation (1)
β = constant in Equation (2), $\alpha R^{5/6}$
λ = thermal conductivity parameter, $M^{1/2}T_c^{1/6}/P_c^{2/3}$
μ = viscosity, g./cm. sec.
μ^* = viscosity at normal pressures, g./cm. sec.
ξ = viscosity parameter, $T_c^{1/6}/M^{1/2}P_c^{2/3}$
ρ = density, g./cc.
ρ_c = critical density, g./cc.
ρ_R = reduced density, ρ/ρ_c

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Manuscript received September 28, 1962; revision received May 16, 1963; paper accepted June 3, 1963.

The Adsorption of Nitrogen-Methane on Molecular Sieves

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Adsorption has been an important method of commercial and laboratory separations. Increasing use of lean natural gas recovery systems and chromatography suggests that adsorption can become a major tool for separations processes rather than a method used, in general, for removal of trace impurities.

The system methane-nitrogen-helium was originally chosen for this work because of the current interest in helium conservation. Equilibrium measurements were then made with the binary system methane-nitrogen. The first experiments showed the adsorption of helium to be virtually negligible.

ADSORPTION THEORY

The customary method of correlating adsorption equilibria involves isothermal treatment of the data. Many adsorption isotherms for single-component systems have been proposed over the years. Among the first was the Freundlich isotherm

$$N = KP^{1/n} \tag{1}$$

In recent years this form has been derived on theoretical grounds (*1*, *24*). The Langmuir isotherm (*11*) in its simplest form

$$N = \frac{aP}{1 + bP} \tag{2}$$

has been widely used to fit isothermal adsorption data and was originally derived from thermodynamic principles assuming adsorption in a single molecular layer. It has been rederived from kinetic (*12*) and statistical (*9*) considerations as well. The equation has also been derived by Schay (*22*) without resorting to the limitation of no molecular interaction present in the original derivations. If the adsorption is multilayer, the more general isotherm of Brunauer, Emmet and Teller (*6*) is a good starting point. More sophisticated approaches seem necessary when dealing with systems where Knudsen flow and internal molecular adsorption exist. In this present study the Langmuir and Freundlich isotherms fitted the data satisfactorily.

Adsorption of multicomponent mixtures has received less attention than pure-component adsorption, although industrial applications commonly deal with mixtures. Markham and Benton (*15*) extended Langmuir's isotherm to mixtures by deriving results in two equations which assume no interaction between the adsorbed components. Schay (*23*) has developed a similar equation which considers interaction of the components and gives a better prediction of adsorption from mixtures especially at higher partial pressures. In the model these interaction coeffici-

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