Viscosity and Thermal Conductivity of Ammonia in The Gaseous and Liquid States

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MOST STUDIES concerned with the transport properties of pure substances have been largely restricted to those of a nonpolar nature. Generalized correlations have been developed that enable the prediction of viscosities (*6, 29*) and thermal conductivities (*12*) from a knowledge of the critical properties of the substance. Although these generalized approaches are valuable contributions for the prediction of approximate values, modern technology requires that these properties be established in a more exacting manner. As a result, attempts have been made to confine these generalizations to groups of substances such as the inert gases (*23, 27*), diatomic gases (*3, 26*), and more complex gases such as carbon dioxide (*17*) and methane (*24*). Although these substances are of increasing molecular complexity, they are not complicated by any polarity effects. In addition, these substances have critical compressibility factors that range from 0.275 to 0.291. Those substances whose z_c-values are less than 0.275 are usually polar in nature. The polarity contributions seem to increase, in general, with decreasing z_c-values. For water, $\mu = 1.831$ debye units (*14*) and $z_c = 0.231$.

Ammonia has been arbitrarily selected for study, since this substance not only possesses a relatively low critical compressibility factor, $z_c = 0.242$, but also a significant dipole moment, $\mu = 1.437$ debye units (*14*).

VISCOSITY AND THERMAL CONDUCTIVITY

Moderate Pressures. For pressures ranging from approximately 1 cc. of mercury to 15 atm. the viscosity and thermal conductivity have been shown to be independent of pressure (*3, 27*). A critical review of the literature has produced experimental viscosity and thermal conductivity data for ammonia that are largely confined to atmospheric pressure.

The dependence of viscosity on temperature is presented in Figure 1 and includes the contributions of ten investigators. Their data are in good agreement and produce a single relationship despite small variations in pressure. These experimental viscosity values are useful in defining the viscosity curve at moderate pressures in the region of $T_R = 0.5$ to $T_R = 1.8$. The extension of this viscosity relationship to higher and lower temperatures has been made possible through the use of the studies of Krieger (*20*) who introduces the contribution of two-point dipoles to the Lennard-Jones potential and arrives at collision integral values, $\Omega^{2,2*}[T_{N_1}\delta^*]$, which are applicable to polar substances.

In the dimensionless polarity parameter, $\delta^* = \frac{1}{2}\mu^2/\epsilon\sigma^3$, introduced by Krieger, the quantity μ represents the polarity of the substance, σ is the collision diameter, and ϵ is the maximum energy of attraction. For ammonia, Krieger reports values of $\sigma = 3.441$A., $\epsilon/k = 146.8°$ K., and $\delta^* = 1.250$. A similar polarity parameter, $\Delta^* = \mu^2/v_cRT_c$, is defined from the polarity and critical constants of the substance. For ammonia, $T_c = 405.5°$ K., $v_c = 72.48$ cc. per gram mole and $\mu = 1.437$ debye units. These values produce a polarity parameter, $\Delta^* = 0.3065$.

Viscosity values for ammonia calculated from the equation

$$[\mu]_1 = 266.93 \times 10^{-5} \frac{(MT)^{1/2}}{\sigma^2\Omega^{2,2*}\,[T_{N_1}\delta^*]} \qquad (1)$$

were found to coincide with the available experimental values. These values allowed the extensions (dash lines in Figure 1 and solid lines in Figure 6) of the viscosity-temperature relationship to cover the range $T_R = 0.2$ to $T_R = 10$.

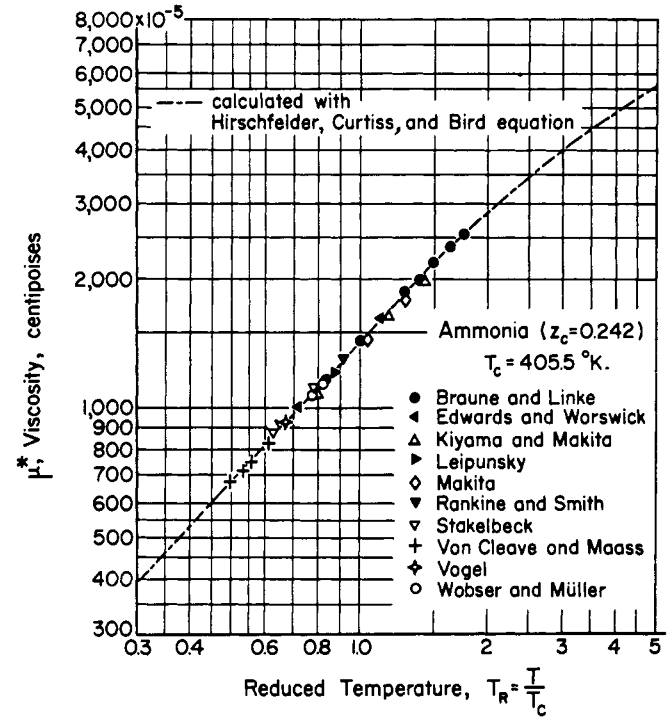

Figure 1. Variation of viscosity with temperature at atmospheric pressure

Available thermal conductivity values for ammonia at essentially atmospheric pressure are presented as a function of reduced temperature in Figure 2. Results of five available sources have been used to produce a relationship that is opposite in curvature to that found to exist for the monatomic and diatomic gases (*23, 26*) when plotted on log-log coordinates. This type of behavior has been exhibited in a similar study for the thermal conductivity of methane (*24*).

The application of the thermal conductivity equation,

$$[k]_1 = 19.891 \times 10^{-5} \frac{(T/M)^{1/2}}{\sigma^2\Omega^{2,2*}\,[T_{N_1}\delta^*]} \qquad (2)$$

when corrected for rotational and vibrational energy contributions (*10*) through the use of the Eucken factor, $\frac{4}{15}\frac{C_v}{R} + \frac{3}{5}$, produced thermal conductivities that were slightly different from the reported experimental values. A plot of log $k_{\text{exptl.}}$ *vs.* log $k_{\text{calcd.}}$ at identical temperatures produced the following relationship:

$$[\log k_{\text{exptl.}}]^{0.5} = 0.574\,[\log k_{\text{calcd.}}] + 0.402 \qquad (3)$$

Equation 2 (corrected with the Eucken factor) combined with Equation 3 allowed the extension of the thermal conductivity-temperature curve to cover the range $T_R =$

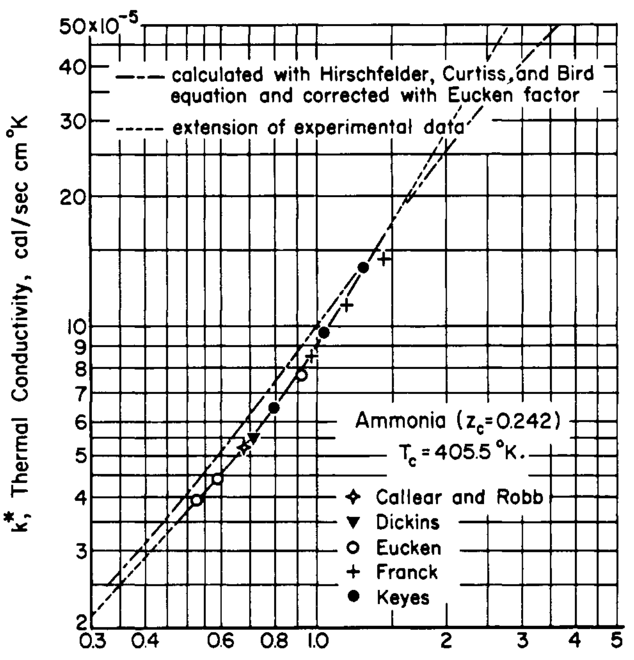

Figure 2. Variation of thermal conductivity with temperature at atmospheric pressure

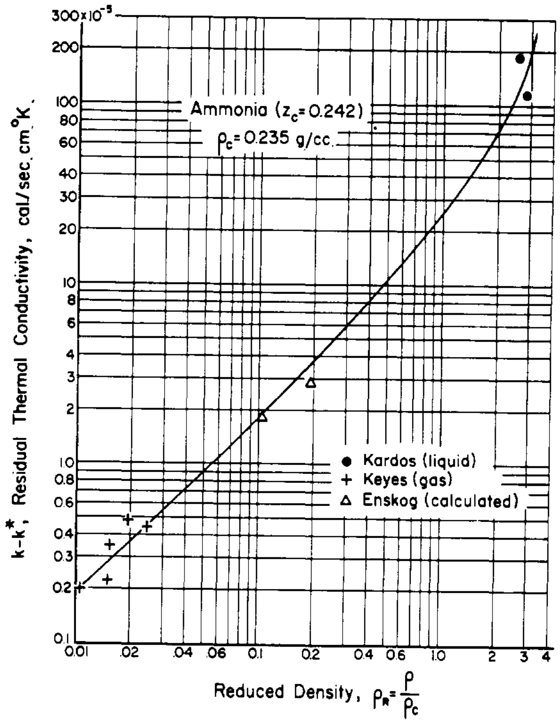

Figure 4. Relationship of residual thermal conductivity and reduced density in the dense phase region

0.30 to T_R = 10. Figures 1 and 2 define the viscosity and thermal conductivity of ammonia at normal pressures through a wide temperature range.

High Pressures. Viscosity and thermal conductivity values at high pressures and for the liquid state were treated along the lines proposed by Abas-Zade (*1*). The residual viscosity and thermal conductivity, $\mu - \mu^*$ and $k - k^*$, were related directly to density of ammonia as shown in Figures 3 and 4, respectively.

High pressure viscosity and thermal conductivity data for ammonia are not plentiful. The available liquid viscosity data of Carmichael and Sage (*5*), because of their internal consistency, offer the best contribution to the study of viscosities in the dense phase region. On the other hand, the gaseous data of Kiyama and Makita (*19*) and Stakelbeck (*28*) appear highly questionable because they exhibited considerable scatter.

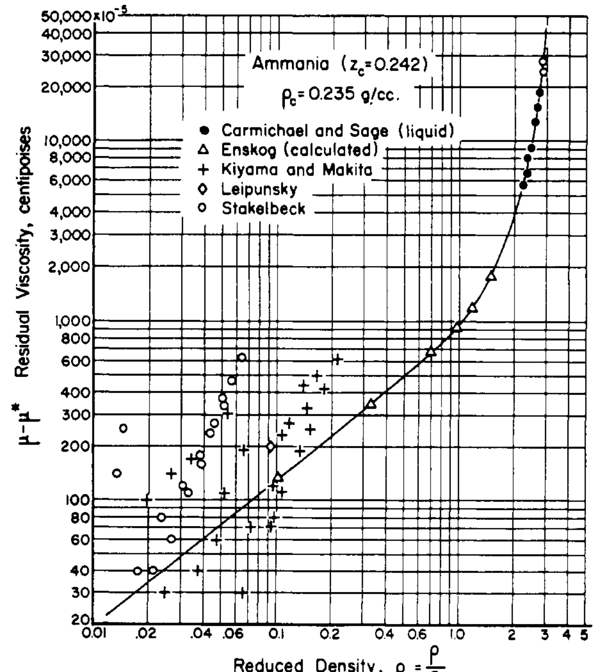

Figure 3. Relationship of residual viscosity and reduced density in the dense phase region

Available data of thermal conductivity at high pressures and for the liquid state are presented by only two sources. Kardos (*16*) presents data for the liquid state while Keyes (*18*) offers some values for the gaseous state at pressures up to 9 atm. This information, although valuable, does not offer a means for completely defining the residual thermal conductivity for a wide range of densities.

Limited experimental data on ammonia for both viscosity and thermal conductivity necessitated the use of the theory of Enskog (*9*) for the calculation of these transport properties at elevated pressures. For viscosity and thermal conductivity Enskog presents the following:

$$\frac{\mu}{\mu^*} = b\rho\left[\frac{1}{b\rho\chi} + 0.800 + 0.7614\, b\rho\chi\right] \qquad (4)$$

$$\frac{k}{k^*} = b\rho\left[\frac{1}{b\rho\chi} + 1.200 + 0.755\, b\rho\chi\right] \qquad (5)$$

The quantities $b\rho\chi$ and the probability of nearness, χ, are defined as

$$b\rho\chi = \frac{z_c}{\rho_R}\left(\frac{\partial P_R}{\partial T_T}\right)_{V_R} - 1 \qquad (6)$$

and

$$\chi = 1 + \tfrac{5}{8}\, b\rho + 0.2869\, (b\rho)^2 \qquad (7)$$

High pressure reduced-density values for ammonia (*13*) were used to obtain values of $b\rho\chi$ over a limited range of temperature. These values of $b\rho\chi$ allowed values of $b\rho$ to be calculated with Equation 7

$$b\rho\chi = b\rho + \tfrac{5}{8}\, (b\rho)^2 + 0.2869\, (b\rho)^3 \qquad (8)$$

This procedure required trial-and-error solutions to obtain values of χ which were used to obtain the quantities $b\rho$ and also values of b. The results for a temperature of T_R = 1.20 are:

P_R	$b\rho\chi$	χ	b
0.46	0.210	1.117	7.833
1.20	0.450	1.264	4.684
2.00	0.700	1.389	3.055
4.00	1.34	1.681	2.271
8.00	1.99	1.949	2.210
20.0	2.81	2.237	2.158
40.0	3.58	2.483	2.127

Substitutions of values of $b\rho$ and $b\rho\chi$, into Equations 4 and 5 allowed the calculation of viscosities and thermal conductivities for regions where no data existed in Figures 3 and 4. The inclusion of viscosity values in Figure 3, calculated with the Enskog method, establishes a unique continuous relationship for the gaseous and liquid states which extends properly into the liquid data of Carmichael and Sage (*5*). From this relationship a critical viscosity value of $\mu_c = 2390 \times 10^{-5}$ centipoise results from a residual value of $(\mu - \mu^*)_c = 950 \times 10^{-5}$ centipoise at the critical density ($\rho_R = 1$) and a corresponding value of $\mu^*_{T_c} = 1440 \times 10^{-5}$ centipoise at atmospheric pressure and $T_R = 1.0$. These values produced a ratio of

$$\frac{\mu_c}{\mu^*_{T_c}} = \frac{2390 \times 10^{-5}}{1440 \times 10^{-5}} = 1.66.$$

In order to establish the relationship of Figure 4, both experimental and calculated residual thermal conductivities for ammonia were compared to those for methane (*24*) at identical reduced densities. The comparison produced a straight line on log-log coordinates in Figure 5. This approach established the single continuous function presented in Figure 4. The residual thermal conductivity relationship of Figure 4 produced a critical thermal conductivity of $k_c = 34.62 \times 10^{-5}$ cal. per sec. cm. ° K. from a residual thermal conductivity of $(k - k^*)_c = 25.6 \times 10^{-5}$ cal. per sec. cm. ° K. and a corresponding value of $k^*_{T_c} = 9.02 \times 10^{-5}$ cal. per sec. cm. ° K. at atmospheric pressure and $T_R = 1.0$. The ratio of $\frac{k^*}{k^*_{T_c}} = \frac{34.62 \times 10^{-5}}{9.02 \times 10^{-5}} = 3.838$.

CONSTRUCTION OF REDUCED STATE CORRELATIONS

The critical viscosity and thermal conductivity values plus the information presented in Figures 1 and 2 established the base isobars for the gaseous state of ammonia at atmospheric pressure expressed in terms of reduced viscosity and reduced thermal conductivity. These properties have been calculated for elevated pressures and for the liquid region by applying densities of ammonia (*13*) for these conditions to the residual viscosities and thermal conductivities presented in Figures 3 and 4. For a selected temperature, viscosities and thermal conductivities were calculated at various pressures by first obtaining the densities corresponding to these conditions to establish values of $\mu - \mu^*$ and $k - k^*$. For this temperature, values of k^* and μ^* were used to produce the actual viscosities and thermal conductivities corresponding to these conditions. Reduced viscosities and thermal conductivities resulted from the division of the actual values by the corresponding critical values and were used to construct Figures 6 and 7. These reduced state correlations for viscosity and thermal conductivity extend to temperatures, $T_R = 10$, and pressures, $P_R = 40$. They also define the saturated vapor and liquid envelopes.

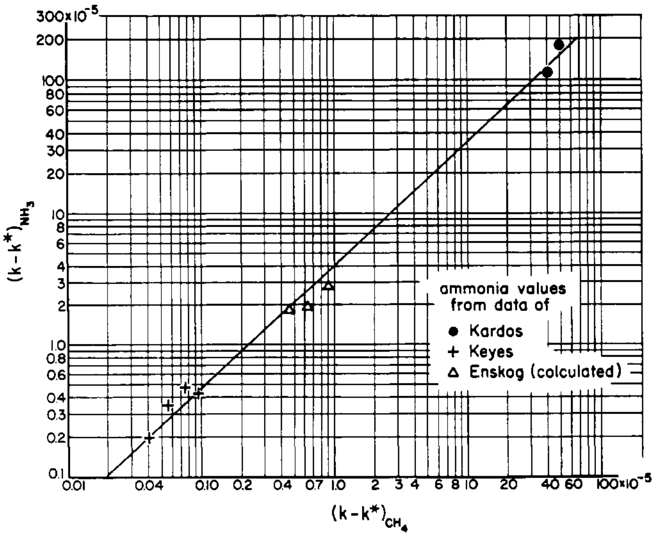

Figure 5. Correlation between residual thermal conductivities and methane at identical reduced densities

The reduced state viscosity correlation is similar to the generalized correlation developed by Uyehara and Watson (*29*) and resembles those presented for the monatomic and diatomic gases (*3, 27*).

The validity of Figure 6 has been tested with all of the available experimental viscosity data. This comparison produced an over-all deviation of 7.61% for 91 points considered. When the data of Kiyama and Makita (*19*) and Stakelbeck (*28*) are omitted, this deviation reduces to 2.9%. This omission is justified, since these data scatter considerably, as shown in Figure 3.

The reduced state thermal conductivity correlation presented in Figure 7 exhibits a pattern that is different from that of the generalized correlation presented by Gamson (*12*) and those for the monatomic and diatomic gases (*23, 26*), but is similar to that exhibited by methane (*24*). The difference of the curvature of the atmospheric pressure line is reflected throughout the entire correlation resulting in this behavior which so far has been exhibited only with polyatomic gases. This thermal conductivity correlation extends to $T_R = 10$, and $P_R = 40$.

The experimental data of Kardos (*16*) and Keyes (*18*) for the dense phase region as well as those for atmospheric pressure (*4, 7, 10, 11, 18*) were compared with values obtained from Figure 7. This comparison showed a deviation of 3.72% for 19 points considered. This correlation for ammonia should also apply to substance having similar critical compressibility factors and substantial polarities.

NOMENCLATURE

b = van der Waals' constant
C_v = heat capacity at constant volume, cal./gram mole ° K.
k = thermal conductivity cal./sec. cm. ° K.
k^* = thermal conductivity at moderate pressures, cal./sec. cm. ° K.
k_c = critical thermal conductivity, cal./sec. cm. ° K.
k_R = reduced thermal conductivity, k/k_c
$k^*_{T_c}$ = thermal conductivity at the critical temperature and moderate pressures, cal./sec. cm. ° K.
M = molecular weight, gram/gram mole
P = pressure, atm.
P_c = critical pressure, atm.
P_R = reduced pressure, P/P_c
R = gas constant, 82.055 atm. cc./gram mole ° K.
T = temperature, ° K.
T_c = critical temperature, ° K.
T_N = normalized temperature, $T/\frac{\epsilon}{\kappa}$
T_R = reduced temperature, T/T_c
v = molar volume, cc./gram mole
v_c = critical molar volume, cc./gram mole
v_R = reduced volume, v/v_c
z = compressibility factor, Pv/RT
z_c = critical compressibility factor, P_cv_c/RT_c

Greek Letters

δ^* = polarity parameter, $\frac{1}{2}\,\mu^2/\epsilon\sigma^3$
Δ^* = polarity parameter, μ^2/v_cRT_c

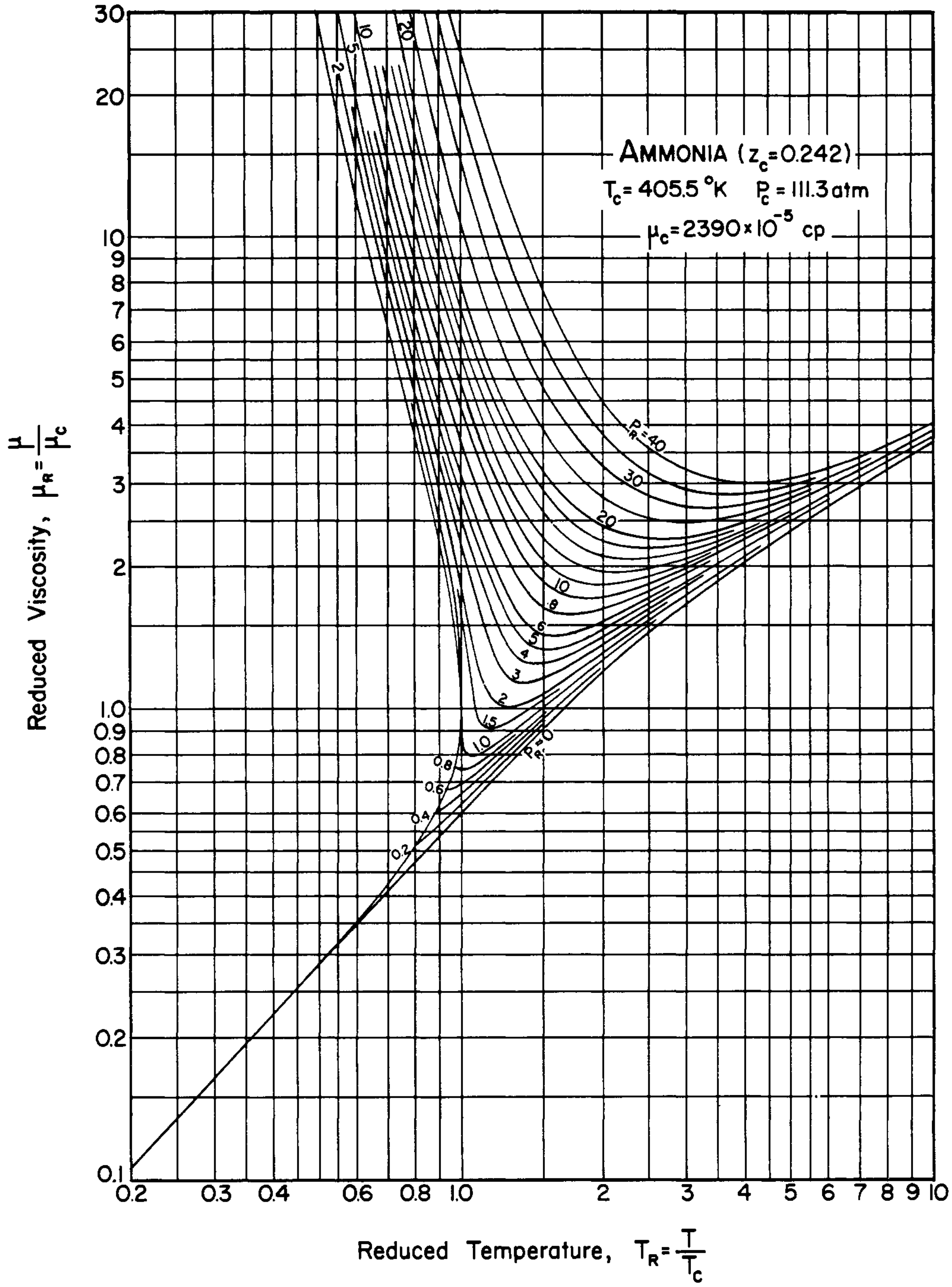

Figure 6. Reduced viscosity correlation

ϵ = maximum energy of attraction for Lennard-Jones potential, ergs
κ = Boltzman constant, 1.3805 × 10^{16} ergs/° K. molecule
μ = polarity, debye units
μ = viscosity, centipoises
μ^* = viscosity at moderate pressures, centipoises
μ_c = critical viscosity, centipoises
μ_R = reduced viscosity, μ/μ_c
$\mu^*_{T_c}$ = viscosity at the critical temperature and moderate pressures, centipoises
ρ = density, gram/cc.
ρ_c = critical density, gram/cc.
ρ_R = reduced density, ρ/ρ_c
σ = collision diameter for Lennard-Jones potential, A.
χ = probability of nearness (Enskog equations)
$\Omega^{2,2*}[T_{N_1}\delta^*]$ = collision integral function for polar molecules

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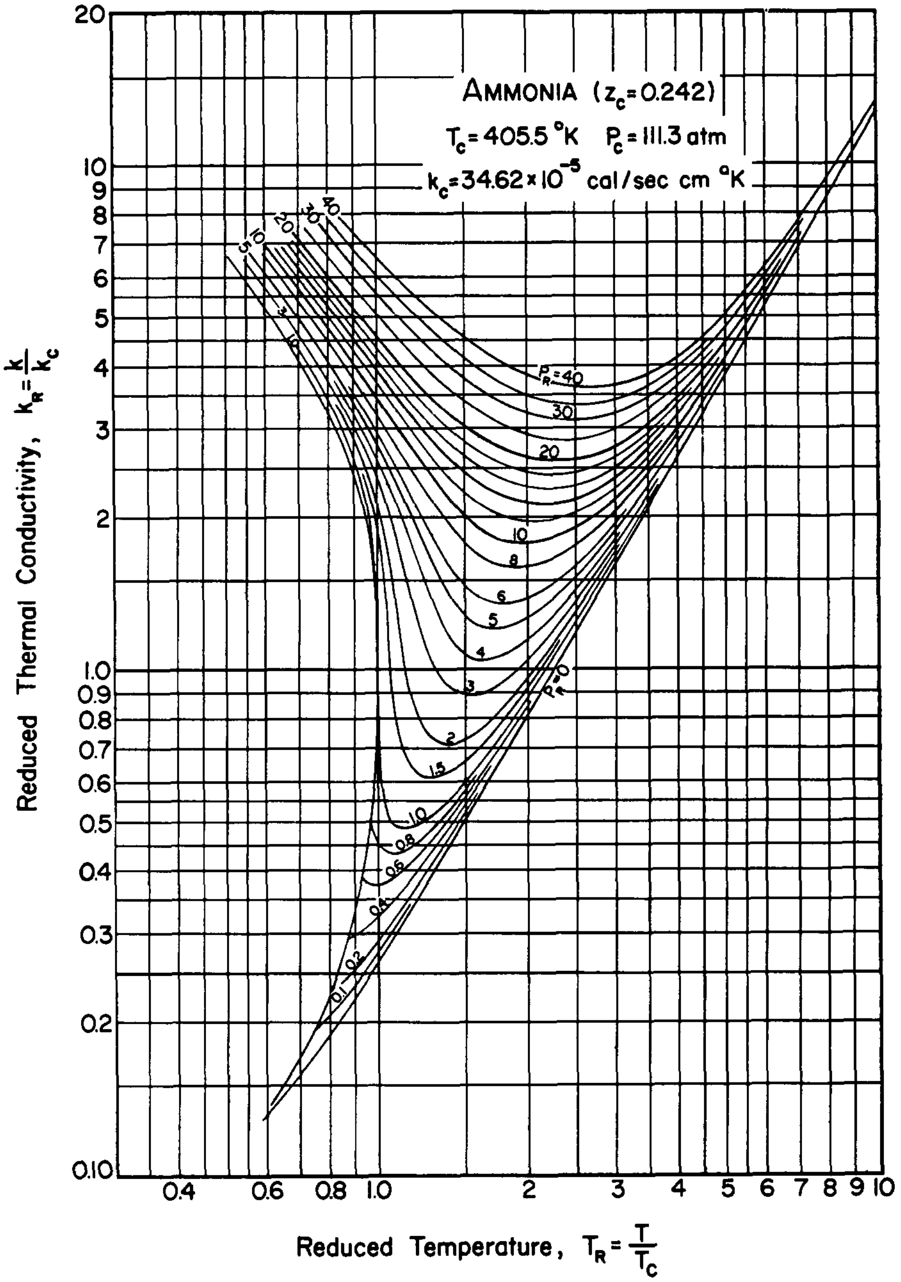

Figure 7. Reduced thermal conductivity correlation

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RECEIVED for review July 21, 1960. Accepted September 19, 1960.