Atmospheric Thermal Conductivities for Gases of Simple Molecular Structure

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The atmospheric thermal conductivity of monatomic, diatomic, and simple polyatomic gases has been related to their molecular weights, critical constants, and heat capacities at constant pressure by the use of available thermal conductivity values for 22 substances. For these substances the quantity $k^*\lambda/C_p^{3/4}$ was found to depend on reduced temperature and the critical compressibility factor. Separate analytical relationships between these quantities were developed for the subcritical, intermediate, and high temperature regions. Individual relationships are presented for helium, hydrogen, and neon, which exhibit excessive quantum deviations. A comparison between experimental thermal conductivities and values calculated by the method of this study produced an over-all average deviation of 2.20% for 851 points.

THE DEMAND for accurate values of the viscosity, thermal conductivity, and self-diffusivity of pure substances has recently fostered considerable activity in the development of relationships for the prediction of these properties. Through a dimensional analysis approach, expressions have been produced which can be used to predict the atmospheric viscosity value at a given temperature for a pure substance from its molecular weight and critical constants (*67, 68*). By a similar approach Misic and Thodos (*47*) have developed relationships for the thermal conductivity of hydrocarbon gases at moderate pressures from available experimental thermal conductivities for 28 hydrocarbons, including normal paraffins, isoparaffins, olefins, diolefins, acetylenes, naphthenes, and aromatics. In this study, the thermal conductivity parameter, $k^*\lambda/C_p^{3/4}$, was found to depend on T_R for all the hydrocarbons investigated.

Hirschfelder, Curtiss, and Bird (*24*) presented the following expression for the thermal conductivity at moderate pressures of nonpolar gases composed of rigid spherical molecules:

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

where the collision integral, $\Omega^{2,2\,*}(T_N)$, is a tabulated function of the normalized temperature, $T_N = T/(\epsilon/\kappa)$ and ϵ and σ are the Lennard-Jones force constants.

Equation 1 has been found to produce accurate thermal conductivity values for the monatomic gases, and the diatomic gases when the values resulting from this equation for these substances were multiplied by the Eucken correction factor for polyatomic molecules, $(4/5)(C_v/R) + (3/5)$. However, this equation has the disadvantage that it requires that accurate viscosity and/or P-V-T data be available to establish the Lennard-Jones force constants of a substance before it can be applied to calculate thermal conductivities. The use of Equation 1 with the Eucken correction factor fails to produce reliable thermal conductivities for triatomic and polyatomic gases, particularly at higher temperatures. Therefore, it would be desirable to use the approach advanced by Misic and Thodos (*47*) for hydrocarbon gases to relate the thermal conductivity of monatomic, diatomic, and simple polyatomic gases to their molecular weights, critical constants, and heat capacities at constant pressure.

TREATMENT OF EXPERIMENTAL THERMAL CONDUCTIVITIES

A comprehensive literature survey was conducted to obtain available experimental thermal conductivity values at atmospheric pressure for 22 substances, including the monatomic and diatomic gases, methane, carbon dioxide, sulfur dioxide, hydrogen sulfide, carbon disulfide, nitrous oxide, ammonia, and water. These substances are listed in Table I, along with their calculated values of λ and the temperature ranges and sources of the experimental thermal conductivities.

For the reported thermal conductivities of each substance, the group $k^*\lambda$ was calculated and plotted against the corresponding heat capacity (*25, 63*) for constant reduced temperatures ranging from $T_R = 0.6$ to $T_R = 6.0$. For the substances having a critical compressibility factor of approximately $z_c = 0.291$, straight lines whose slopes were approximately $3/4$ resulted for each reduced temperature. Therefore, for each substance the quantity $k^*\lambda/C_p^{3/4}$ was plotted against reduced temperature on log-log coordinates. The resulting relationships were found to depend on the critical compressibility factors of the substances, and a single relationship was obtained for those substances having $z_c \approx 0.291$, as shown in Figure 1. In Figure 2 are presented the relationships for the other substances for which ssufficient thermal conductivities are available.

For helium, hydrogen, and neon, separate curves were obtained despite the fact that these substances have approximately the same critical compressibility factor ($z_c \approx 0.306$). This behavior results from excessive quantum deviations exhibited by these substances. On the other hand, bromine ($z_c \approx 0.306$) follows the behavior of other substances which do not exhibit quantum effects.

The relationships of Figures 1 and 2 could not be easily expressed analytically over the complete range of reduced temperatures. Therefore, separate relationships for each substance were obtained for the subcritical, intermediate, and high temperature ranges.

Subcritical Region ($T_R < 1.00$). For the subcritical region, values of $(k^*\lambda/C_p^{3/4})^n$ for each substance were plotted against reduced temperature to establish the exponents n for which linear relationships on rectilinear coordinates

Table I. Values of Parameter λ, Temperature Ranges, Sources of Thermal Conductivities, and Average Deviations

	z_c	λ	T_c, ° K.	T_R	Points	Deviation, %	References
Helium	0.306	1.529	5.206	0.75-184	44	1.84	*(7, 8, 9, 28, 29, 32, 42, 53, 71, 77, 90)*
Neon	0.307	0.942	44.45	2-13	21	1.57	*(29, 30, 32, 36, 71, 90)*
Argon	0.291	1.104	150.7	0.60-6.3	52	1.20	*(8, 26, 29, 30, 32, 36, 37, 42, 43, 45, 58, 60, 78, 85, 89, 90)*
Krypton	0.292	1.555	209.4	0.62-2.75	12	1.74	*(29, 37)*
Xenon	0.290	1.967	289.75	0.67-2.0	9	1.73	*(29, 37)*
Hydrogen	0.305	0.465	33.3	0.51-21.4	118	1.52	*(1, 3, 7, 8, 9, 11, 17, 18, 26, 28, 32, 42, 51, 55, 58, 59, 69, 75, 76, 81, 88, 89, 91, 94)*
Nitrogen	0.291	1.141	126.2	0.65-8.5	144	2.34	*(1, 4, 5, 7, 8, 9, 12, 21, 26, 27, 35, 37, 38, 42, 50, 54, 60, 69, 73, 78, 79, 80, 82, 89, 92)*
Oxygen	0.293	0.965	154.8	0.56-5.1	77	2.75	*(1, 4, 5, 7, 8, 9, 11, 12, 17, 28, 32, 37, 49, 73, 88, 89, 95)*
Carbon Monoxide	0.294	1.127	133	0.61-2.85	38	1.70	*(1, 7, 9, 16, 19, 26, 28, 32, 56)*
Nitric Oxide	0.251	0.814	180	0.67-2.7	21	0.93	*(1, 9, 28, 52, 56, 73)*
Fluorine		1.411	144	0.69-6.90			*(12, 14)*
Chlorine	0.275	1.281	417.2	0.47-1.62	11	2.52	*(10, 14)*
Bromine	0.307	1.674	584	0.48-1.88	4	1.05	*(12, 14)*
Hydrogen Fluoride		0.608	503.4	1.56			*(13, 15)*
Hydrogen Chloride	0.266	0.842	324.5	0.61-1.78	5	11.72	*(12)*
Hydrogen Bromide		1.252	363.2	0.53-1.36			*(12)*
Carbon Disulfide	0.298	1.369	552	0.49	2	1.08	*(1, 9)*
Hydrogen Sulfide	0.282	0.787	373.6	0.73	1	13.2	*(9)*
Carbon Dioxide	0.275	0.987	304.2	0.61-3.53	121	2.26	*(1, 2, 6, 7, 8, 9, 12, 20, 26, 28, 30, 31, 32, 34, 35, 37, 42, 53, 54, 56, 61, 62, 66, 69, 70, 71, 73, 74, 89, 91)*
Nitrous Oxide	0.271	1.000	309.7	0.61-1.22	7	1.71	*(1, 9, 28, 30, 32, 89)*
Sulfur Dioxide	0.269	1.207	430.7	0.63	1	8.53	*(9)*
Water	0.231	0.344	647.4	0.42-1.95	111	2.79	*(10, 11, 33, 38, 40, 46, 48, 57, 72, 79, 80, 83, 84, 86, 87)*
Hydrogen Cyanide	0.197	1.020	456.7	0.61-1.06	4	4.61	*(12)*
Ammonia	0.242	0.485	405.5	0.67-1.43	7	0.96	*(7, 9, 12, 22)*
Methane	0.289	0.749	191.1	0.63-4.05	31	3.48	*(9, 23, 28, 36, 37, 41, 42, 43, 44, 60, 64, 65, 69, 89, 90, 93, 96)*

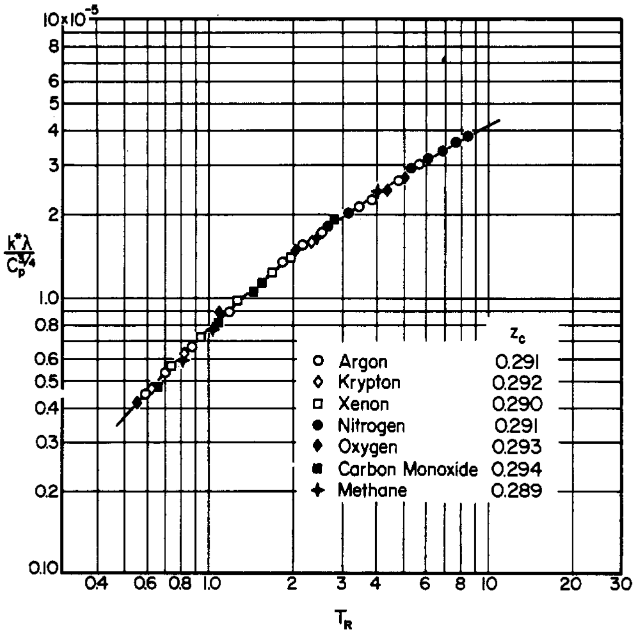

Figure 1. Relationship between $k^*\lambda/C_p^{3/4}$ and T_R for substances having critical compressibility factors of $z_c \approx 0.291$

resulted. The resulting straight lines converged at the origin and could be represented analytically as follows:

$$\frac{k^*\lambda}{C_p^{3/4}} \times 10^6 = (\alpha T_R)^m \qquad (2)$$

where $m = 1/n$. The exponent m was found to vary linearly with the critical compressibility factor of the substances as follows:

$$m = 1.810 - 2.604 z_c \qquad (3)$$

Similarly, α was found to have the following dependence on z_c:

$$\alpha = 20.0 z_c + 1.08 \qquad (4)$$

Intermediate Region (1.00 $\leqq T_R <$ 3.00). A similar procedure was employed to determine analytical relationships of the following form for the intermediate region:

$$\frac{k^*\lambda}{C_p^{3/4}} \times 10^6 = (\beta T_R + \delta)^p \qquad (5)$$

Again the exponent p was found to vary linearly with z_c as follows:

$$p = 1.524 - 2.800 z_c \qquad (6)$$

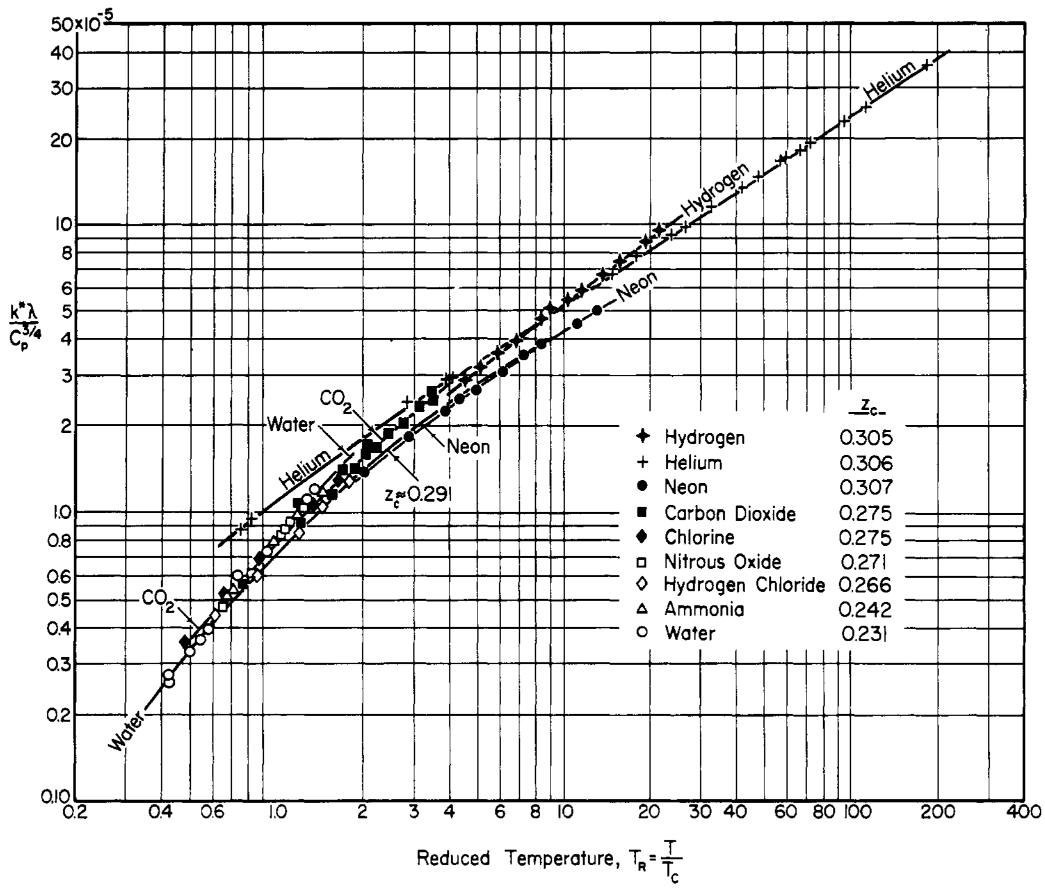

Figure 2. Relationships between $k^*\lambda C_p^{3/4}$ and T_R for substances having critical compressibility factors, $0.231 \approx z_c \approx 0.307$

When β and δ were plotted against z_c for each substance, straight lins resulted which can be expressed analytically as:

$$\beta = 195 z_c - 31.94 \qquad (7)$$

and.

$$\delta = 16.83 - 82.5 z_c \qquad (8)$$

High Temperature Region ($3.00 \leqq T_R < 15.0$). For the high temperature region relationships of the following form were obtained for the substances for which experimental data were available:

$$\frac{k^*\lambda}{C_p^{3/4}} \times 10^5 = (\gamma T_R + \epsilon)^s \qquad (9)$$

The following linear relationships between z_c and s, γ, and ϵ were established for this region:

$$s = 1.079 - 1.97 z_c \qquad (10)$$

$$\gamma = 7.18 - 18.25 z_c \qquad (11)$$

$$\epsilon = 10.21 z_c - 4.91 \qquad (12)$$

The thermal conductivity at the boundary between the subcritical and intermediate temperature regions ($T_R = 1.00$) can be calculated with Equations 2 and 5 and between the intermediate and high temperature regions ($T_R = 3.00$) can be calculated with Equations 5 and 9. The corresponding computed values are in close agreement and produce an average deviation of 1.4% for the substances included in this investigation when experimental thermal conductivities are available at these boundaries.

Experimental data were also available for fluorine (*12, 14*), hydrogen fluorine (*13, 15*), and hydrogen bromide (*12*), but could not be included in this study since the critical compressibility factors of these substances are not known. Nitric oxide and hydrogen cyanide, whose critical constants are of uncertain reliability, were found to deviate from the general behavior exhibited by the other substances when values of the exponents m and p were calculated for these substances from Equations 3 and 6. Corrected values of the exponents, which enable accurate thermal conductivity values to be calculated for these substances, were determined from experimental data to be for hydrogen cyanide $m = 1.425$ and for nitric oxide $m = 1.082$ and $p = 0.765$. Consequently, these values should be used with Equations 2 and 5 to produce thermal conductivities which are in close agreement with the experimental values of these substances.

The method developed in this study for the calculation of thermal conductivities is illustrated with the following example.

Example: Calculate the thermal conductivity of CO_2 at 200° C. and atmospheric pressure. The heat capacity of CO_2 at these conditions is 10.53 cal./gram-mole ° K.

From Table I, for CO_2 $T_c = 304.2°$ K. and $z_c = 0.275$. At 200° C., $R_R = 473.2/304.2 = 1.556$. Therefore, Equations 5 to 8 should be used:

$$\frac{k^*\lambda}{C_p^{3/4}} \times 10^6 = (\beta T_R + \delta)^p$$

$$p = 1.524 - 2.800 z_c = 0.754$$

$$\beta = 195 z_c - 31.94 = 21.68$$

$$\delta = 16.83 - 82.5 z_c = -5.86$$

From Table I, $\lambda = 0.987$ for CO_2. Therefore,

$$\frac{k^*(0.987)}{(10.53)^{3/4}} \times 10^6 = [21.68(1.556) - 5.86]^{0.754}$$

or

$$k^* = 72.8 \times 10^{-6} \text{ cal./sec. cm. } ^\circ\text{K.}$$

At these conditions, Rothman and Bromley *(54)* report a value of $k^* = 72.0 \times 10^{-6}$ cal./sec. cm. °K. for CO_2. Thus, the agreement between the calculated and reported value is well within the experimental error.

Substances Exhibiting Quantum Effects. Since a single relationship did not result for helium, neon, and hydrogen despite the fact that these substances have similar critical compressibility factors, it was found necessary to establish individual relationships for these substances. For helium, the following equations accurately represent the thermal conductivity for $T_R < 2.00$:

$$k^* \times 10^5 = 2.04 \times T_R \qquad T_R < 1.00 \qquad (13a)$$

$$k^* \times 10^5 = [4.34\,T_R - 1.42]^{2/3} \qquad 1.0 \leqq T_R < 3.0 \qquad (13b)$$

$$k^* \times 10^5 = [3.83\,T_R + 0.10]^{2/3} \qquad 3.0 \leqq T_R < 15 \qquad (13c)$$

$$k^* \times 10^5 = 2.581\,T_R^{0.654} \qquad 15 \leqq T_R < 200 \qquad (13d)$$

For neon, the following equations can be used to calculate the thermal conductivity behavior for $1.0 < T_R < 15$:

$$k^* \times 10^5 = [6.58\,T_R - 2.24]^{2/3} \qquad 1.0 \leqq T_R < 3.0 \qquad (14a)$$

and

$$k^* \times 10^5 = [5.87\,T_R - 0.11]^{2/3} \qquad 3.0 \leqq T_R < 15 \qquad (14b)$$

Similarly, the following equations represent the dependence of thermal conductivity on reduced temperature for hydrogen:

$$k^* \times 10^5 = 5.40\,T_R \qquad T_R < 1.0 \qquad (15a)$$

$$k^* \times 10^5 = [10.11\,T_R - 2.53]^{0.833} \qquad 1.0 \leqq T_R < 3.0 \qquad (15b)$$

$$k^* \times 10^5 = [16.52\,T_R - 12.66]^{0.769} \qquad 3.0 \leqq T_R < 20 \qquad (15c)$$

The application of Equations 13, 14, and 15 is necessary since Equations 2, 5, and 9 do not include a parameter that accounts for the anamolous behavior of substances exhibiting quantum effects.

RESULTS

For the substances investigated, thermal conductivity values were calculated with the appropriate equations by the outlined methods and were compared with the corresponding experimental values. The resulting average deviation for each substance is presented in Table I. For 851 experimental points the overall average deviation was 2.20%. Since this deviation is of the same order of magnitude as the experimental error of thermal conductivity, heat capacity, and critical constants *(39)*, the method developed in this study is capable of predicting accurately thermal conductivity values at atmospheric pressure for substances having simple molecular structure.

NOMENCLATURE

C_p = heat capacity at constant pressure, cal./gram-mole °K.
C_v = heat capacity at constant volume, cal./gram-mole °K.
$[k]_1$ = first approximation of thermal conductivity, cal./sec. cm. °K.
k^* = thermal conductivity at normal pressures, cal./sec. cm. °K.
m = exponent for Equation 2
M = molecular weight
p = exponent for Equation 5
P_c = critical pressure, atm.
R = gas constant
s = exponent for Equation 9
T = temperature, °K.
T_c = critical temperature, °K.
T_N = normalized temperature. $T/(\epsilon/\kappa)$
T_R = reduced temperature, T/T_c
v_c = critical volume, cc./gram-mole
z_c = critical compressibility factor, $P_c v_c/RT_c$
α, β, γ = temperature coefficients for Equations 4, 7, and 11, respectively
δ, ϵ = constants for Equations 7 and 11
ϵ = maximum energy of attraction for Lennard-Jones potential, ergs
κ = Boltzmann constant, 1.3805×10^{-16} erg/°K.
λ = characteristic constant, $T_c^{1/6}/M^{1/2}P_c^{2/3}$
σ = collision diameter for Lennard-Jones potential, A.
$\Omega^{2,2*}[T_N]$ = collision integral function

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Vapor Pressures of Silicon Tetrachloride–Titanium Tetrachloride Mixtures

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Liquid phase activity coefficients for silicon tetrachloride–titanium tetrachloride solutions are presented. The activity coefficients were calculated from total pressure–composition data for the 30°, 40°, and 50° C. isotherms. The results have been correlated using the two suffix van Laar equations.

LIQUID PHASE activity coefficients for silicon tetrachloride–titanium tetrachloride solutions are presented. The activity coefficients were calculated from total pressure–composition data for the 30°, 40°, and 50° C. isotherms with glass Bourdon tubes serving as the pressure sensing elements. The results have been correlated using the two suffix van Laar equations. The van Laar constants, *A* and *B*, were determined so as to give a "least-squares fit" to the data.

EXPERIMENTAL COMPOUNDS

Chemicals used were Fisher Scientific technical grade silicon tetrachloride, Fisher Scientific purified grade titanium tetrachloride, and Fisher Scientific reagent grade carbon tetrachloride.

PROCEDURE AND APPARATUS

Because both silicon tetrachloride and titanium tetrachloride react with the water vapor in air, it was necessary