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Thermal Conductivity of Gaseous Air at Moderate and High Pressures

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Values of the thermal conductivity of air have been established for temperatures to 800° K. and pressures to 1000 atm. Reported thermal conductivity values for air at atmospheric pressure were related to temperature. Thermal conductivity values for nitrogen were used to establish a relationship between the reduced residual thermal conductivity, $(k - k^*)\lambda$, and reduced density. This relationship enabled thermal conductivity values to be established for gaseous air for a complete range of temperatures and pressures. The values from this study were compared with those resulting from a recent Russian investigation.

VALUES of the thermal conductivity of gaseous air are required for many design applications. Only meager experimental thermal conductivity data are available for this substance for the dense gaseous region. Granet and Kass (*8*) have used the generalized correlation of Gamson (*6*) to develop a plot of the thermal conductivity of air as a function of temperature and pressure for pressures to 2000 p.s.i.a. In a recently translated Russian book on the thermal conductivity of gases and liquids, Tsederberg (*25*) presented calculated values of the thermal conductivity of air for temperatures to 1000° C. and pressures to approximately 200 atm. In the present study, an alternate analysis based on the theorem of corresponding states has been used to establish values of the thermal conductivity of air for temperatures to 800° K. and pressures to 1000 atm. A similar study on the viscosity of gaseous air has recently been reported by Lo, Carroll, and Stiel (*17*).

THERMAL CONDUCTIVITY OF AIR AT MODERATE PRESSURES

Keyes (*16*) fitted the available data for the thermal conductivity of gaseous air at moderate pressure (approximately 1 atm.) for the temperature range 90° to 584° K. to the equation

$$k^* = \frac{0.632 \times 10^{-5} [T]^{1/2}}{1 + \frac{245}{T} \times 10^{-12/T}} \qquad (1)$$

Hilsenrath *et al.* (*12*) tabulated values of the thermal conductivity of air calculated from Equation 1 for temperatures from 80° to 1000° K. They assessed the reliability of the calculated values as being within 4%; however, the values for 590° to 1000° K. involved an extrapolation of Equation 1 beyond the range of the data utilized in its development. Glassman and Bonilla (*7*) found that their experimental values of the thermal conductivity of air for temperatures to 730° K. agreed with values calculated from Equation 1 to within 1% over the region investigated. Vines (*28*) measured thermal conductivity values for air from temperatures from 240° to 900° C. and found that the experimental values were in substantial agreement with the tabulated values of Hilsenrath *et al.* for temperatures to 750° C. but were slightly higher for temperatures above 750° C.

In the present study, experimental values of the thermal conductivity of air at moderate pressure, k^*, reported by 19 investigators, were obtained from the literature. The sources are listed in Table I with the temperature ranges investigated. In Figure 1, representative data from all the investigators are plotted against temperature for the range 80° to 1200° K. Most of the data are consistent and enable the thermal conductivity behavior of air to be established for this region.

The data reported by all of the investigators were approximated by a fifth order polynomial using a least squares procedure with orthogonal polynomials. The resulting equation is

$$k^* = -1.116 + 4.030 \times 10^{-2}T - 8.941 \times 10^{-5}T^2 + 1.661 \times 10^{-7}T^3 - 1.468 \times 10^{-10}T^4 + 4.729 \times 10^{-14}T^5 \quad (2)$$

where k^* is in calories per centimeter second ° C. Thermal conductivity values were calculated from Equation 2 for each experimental point. The resulting standard error of estimate for each investigator is shown in Table I. The standard error of estimate for the 148 points is 0.223×10^{-5} cal. per centimeter second ° C.

THERMAL CONDUCTIVITY BEHAVIOR IN THE DENSE GASEOUS REGION

The only experimental thermal conductivity data available for air in the dense gaseous region are those of Stolyarov, Ipatiev, and Teodorovich (*22*) for temperatures from 20° to 180° C. and pressures from 1 to 390 atm. However, for nitrogen in the dense gaseous region the data of these investigators deviate by as much as 10% from those of other investigators.

Isotherms of the thermal conductivity of dense gases against density are parallel, indicating that a unique relationship should exist between $k - k^*$ and density, where k is the thermal conductivity of a gas at a given temperature and pressure and k^* is the thermal conductivity of the gas at the same temperature and atmospheric pressure. Tsederberg (*25*) assumed a relationship of the form

$$k - k^* = B\rho^n \quad (3)$$

for reduced densities less than $\rho_R = 1.5$. Exponent n for air was calculated from a linear relationship between n and molecular weight obtained from experimental data for hydrogen, helium, methane, water, nitrogen, oxygen, argon, carbon dioxide, methanol, ethanol, benzene, toluene, and xylene. Coefficient B was evidently determined from the experimental data of Stolyarov, Ipatiev, and Teodorovich (*22*).

In the present study, a corresponding states approach has been used to establish the thermal conductivity behavior of air in the dense gaseous region. Stiel and Thodos (*21*) developed the following relationship through dimensional analysis considerations:

$$(k - k^*)\lambda = f(\rho_R, z_c) \quad (4)$$

where

$$\lambda = M^{1/2}T_c^{1/6}/P_c^{2/3}$$

For nitrogen for temperatures from 75° to 700° C. and pressures to 1500 atm., the thermal conductivity data of Johanin (*13*) represent some of the most accurate high pressure data available. Since nitrogen and air have essentially the same value of the critical compressibility factor, the experimental data of Johanin for nitrogen can be employed to establish thermal conductivity values for air through the use of Equation 4 with $(k - k^*)\lambda$ as a function of only ρ_R. Therefore, values of $(k - k^*)\lambda$ resulting from the data of Johanin were plotted against ρ_R on log-log coordinates (Figure 2). Figure 2 shows that a unique relationship is obtained but that this relationship is not linear on log-log coordinates for $\rho_R > 1.5$ as maintained by Tsederberg (*25*) and indicated by Equation 3. The experimental data of Stolyarov, Ipatiev, and Teodorovich (*22*) deviated considerably from the relationship of Figure 2. The data values of Figure 2 were approximated by the following equation through a least squares procedure.

$$(k - k^*)\lambda = 0.304 + 6.75D_R - 5.13D_R^2 + 25.45D_R^3 - 21.67D_R^4 + 7.32D_R^5 \quad (5)$$

where

$$D_R = \frac{\rho_R - 0.10}{1.62 - 0.10}$$

Table I. Sources of Thermal Conductivity Data and Average Deviations for Air at Atmospheric Pressure

	Number of Points	Temperature Range, ° K.	Standard Error[a] of Estimate, (Cal./Cm. Sec. ° C.) × 10^{-5}
Sherratt and Griffiths (*20*)	24	333–593	0.099
Dickins (*3*)	2	273–285	0.025
Gregory and Archer (*9*)	1	273	0.260
Vines (*27*)	4	304–383	0.144
Kannuluik and Carman (*14*)	5	90–491	0.222
Euken (*5*)	4	90–373	0.231
Masia and Roig (*18*)	7	277–406	0.170
Stolyarov, Ipatiev, and Teodorovich (*22*)	4	297–472	0.232
Vargaftik and Oleshchuk (*26*)	3	273–1073	0.137
Hercus and Laby (*10*)	4	273–285	0.017
Hercus and Sutherland (*11*)	10	293	0.400
Vines (*28*)	4	513–1173	0.287
Milverton (*19*)	8	277–366	0.063
Kannuluik and Martin (*15*)	1	276	0.061
Weber (*29*)	1	273	0.179
Boelter and Sharp (*1*)	39	278–760	0.224
Taylor and Johnston (*24*)	17	88–376	0.172
Stops (*23*)	6	533–768	0.443
Glassman and Bonilla (*7*)	4	400–700	0.313

[a] Standard error of estimate $= \left[\left\{\sum_1^N (k^*_{\text{exp}} - k^*_{\text{calcd}})^2\right\}/N\right]^{1/2}$.

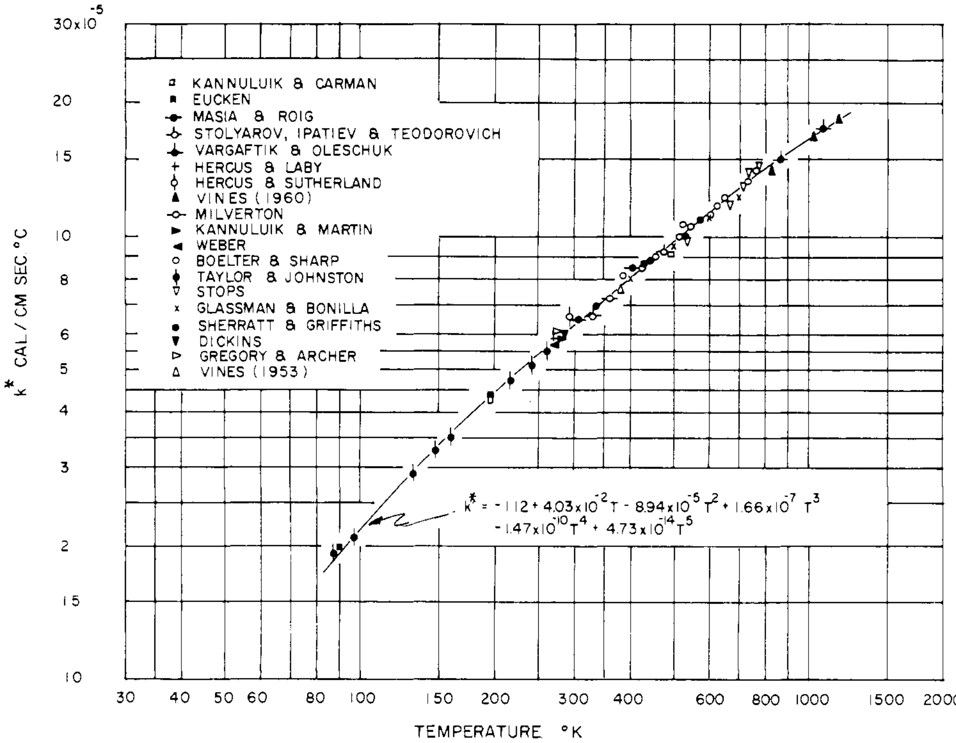

Figure 1. Relationship between thermal conductivity and temperature for air at moderate pressures

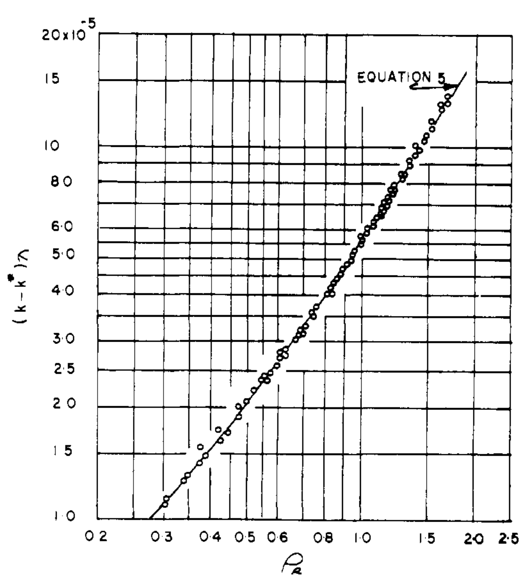

Figure 2. Relationship between $(k - k^*)\lambda$ and ρ_R for nitrogen
Data from Johanin (*13*)

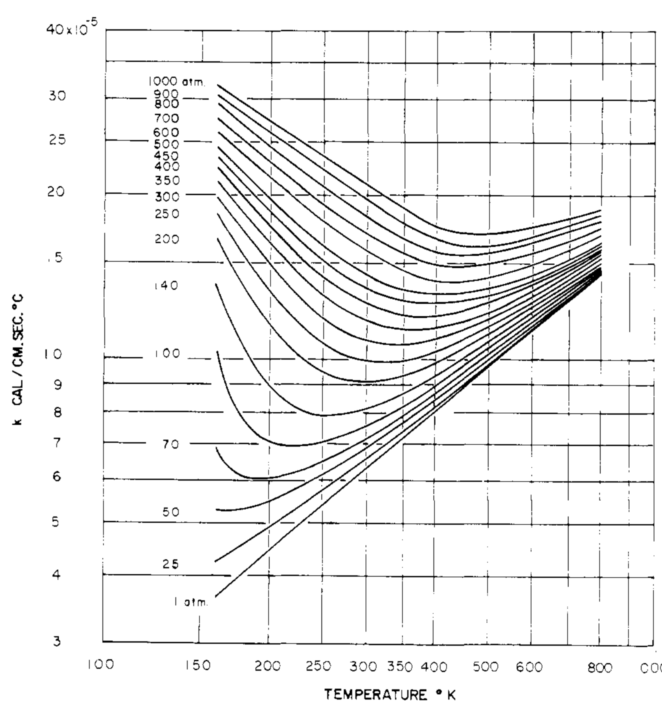

Figure 3. Thermal conductivity correlation for air in gaseous region

The maximum average per cent error between values calculated from Equation 5 and the corresponding experimental values of Johanin (*13*) was 2.15%. This agreement is considered to be very good since the accuracy of the experimental data of Johanin is claimed to be within 1.5%, and additional error is introduced through the use of density and k^* data.

Thermal conductivity values for air were calculated from Equation 5 for temperatures from 160° to 800° K. and pressures to 1000 atm. Values of k^* for this temperature range were calculated from Equation 2. Density values for air were obtained from the tabulations of Hilsenrath *et al.* (*12*) and of Din (*4*) and at high temperatures from the reduced state density correlation by Byrne and Thodos (*2*) for diatomic gases by the use of pseudocritical constants for air. A plot of the thermal conductivity of air against temperature and pressure is presented in Figure 3. Thermal conductivity values for even intervals of temperature and

Table II. Thermal Conductivity Values of Gaseous Air, Cal./Sec. Cm. ° C.

Press., Atm.	160° K.	180° K.	200° K.	220° K.	240° K.	260° K.	280° K.	300° K.	320° K.	340° K.	360° K.
1	3.632	4.064	4.476	4.871	5.252	5.622	5.983	6.337	6.686	7.031	7.373
25	4.24	4.56	4.89	5.23	5.56	5.90	6.23	6.57	6.88	7.21	7.54
50	5.29	5.28	5.47	5.73	6.00	6.29	6.60	6.91	7.19	7.50	7.82
70	6.91	6.06	6.02	6.16	6.37	6.61	6.88	7.17	7.44	7.73	8.03
100	10.34	7.74	7.06	6.92	6.97	7.12	7.33	7.57	7.80	8.06	8.34
140	13.47	10.35	8.82	8.16	7.93	7.90	7.98	8.14	8.30	8.52	8.76
200	16.46	13.46	11.46	10.25	9.58	9.23	9.10	9.10	9.15	9.27	9.44
250	18.31	15.44	13.36	11.92	10.97	10.42	10.11	9.98	9.92	9.96	10.06
300	19.85	17.04	14.96	13.41	12.32	11.59	11.14	10.89	10.72	10.68	10.71
350	21.19	18.43	16.34	14.74	13.55	12.71	12.15	11.79	11.54	11.40	11.37
400	22.44	19.69	17.56	15.90	14.68	13.77	13.11	12.67	12.37	12.13	12.02
450	23.54	20.76	18.60	17.00	15.70	14.74	14.03	13.43	13.04	12.91	12.74
500	24.46	21.65	19.48	18.00	16.66	15.68	14.90	14.35	13.89	13.36	13.26
600	26.19	23.74	21.50	19.74	18.38	17.36	16.51	15.87	15.34	14.73	14.38
700	27.74	24.95	22.75	21.32	19.93	18.86	17.94	17.08	16.40	16.02	15.52
800	29.89	26.45	24.30	22.64	21.39	20.23	19.28	18.28	17.46	16.83	16.48
900	30.21	27.80	25.80	24.14	22.71	21.53	20.60	19.75	19.04	18.19	17.53
1000	31.84	29.21	27.25	25.34	23.85	22.82	21.83	20.97	20.04	19.38	18.66

Press., Atm.	380° K.	400° K.	450° K.	500° K.	550° K.	600° K.	650° K.	700° K.	750° K.	800° K.
1	7.714	8.054	8.901	9.746	10.583	11.405	12.20	12.957	13.66	14.313
25	7.86	8.17	9.01	9.77	10.65	11.44	12.25	12.97	13.63	14.31
50	8.12	8.43	9.24	10.13	10.85	11.61	12.42	13.13	13.78	14.46
70	8.32	8.62	9.41	10.32	11.02	11.77	12.56	13.27	13.90	14.56
100	8.61	8.89	9.65	10.53	11.21	11.95	12.71	13.40	14.05	14.71
140	9.00	9.25	9.98	10.80	11.47	12.17	12.95	13.63	14.25	14.92
200	9.63	9.84	10.47	11.25	11.84	12.46	13.23	13.85	14.51	15.16
250	10.19	10.37	10.93	11.62	12.15	12.77	13.50	14.17	14.79	15.40
300	10.78	10.90	11.35	12.00	12.43	13.07	13.75	14.36	14.95	15.59
350	11.38	11.47	11.84	12.42	12.85	13.41	14.05	14.68	15.24	15.84
400	12.00	12.00	12.41	12.85	13.17	13.69	14.31	14.88	15.42	15.99
450	12.71	12.68	12.85	13.17	13.49	13.98	14.52	15.05	15.63	16.24
500	13.08	13.08	13.22	13.52	13.85	14.29	14.81	15.33	15.82	16.43
600	14.05	13.75	13.87	14.12	14.56	14.85	15.38	15.92	16.36	16.96
700	15.21	15.00	14.75	15.00	15.32	15.70	16.13	16.56	16.90	17.49
800	16.04	15.74	15.55	15.72	16.02	16.50	16.88	17.20	17.53	17.90
900	17.04	16.59	16.02	16.17	16.42	16.90	17.42	17.75	18.00	18.50
1000	18.01	17.50	16.93	17.09	17.17	17.63	17.93	18.24	18.57	18.87

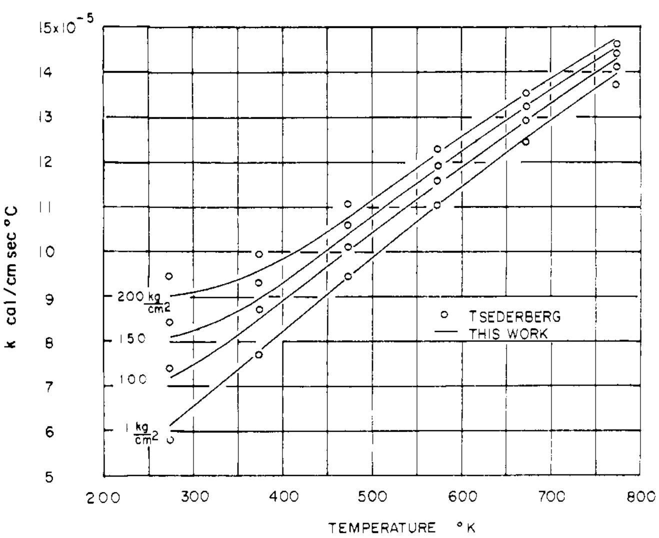

Figure 4. Comparison of values of Tsederberg (25) with those from this work

pressure are presented in Table II. Thermal conductivity values for nitrogen and oxygen can also be calculated directly from Equation 5.

In Figure 4, the thermal conductivity values of Tsederberg (*25*) for pressures to 200 kg. per sq. cm. are compared with those resulting from this study. The maximum per cent error between the values from both studies is 5%. The agreement is good for temperatures higher than 500° K.

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NOMENCLATURE

- B = constant in Equation 3
- D_R = normalized reduced density $(\rho_R - 0.10)/(1.62 - 0.10)$
- k = thermal conductivity, cal./sec. cm. ° C.
- k^* = thermal conductivity at atmospheric pressure, cal./sec. cm. ° K.
- M = molecular weight
- n = exponent in Equation 3
- N = number of points
- P_c = critical pressure, atm.
- T = temperature, ° K.
- T_c = critical temperature, ° K.
- z_c = critical compressibility factor

Greek Letters

- λ = thermal conductivity parameter, $M^{1/2}T_c^{1/6}/P_c^{2/3}$
- ρ = density, g./cc.
- ρ_c = critical density, g./cc.
- ρ_R = reduced density, ρ/ρ_c

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Reduced State Correlation for the Enskog Modulus Developed from *PVT* Data for Ethane

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PVT data available in the literature for ethane have been utilized to establish the Enskog modulus, $b\rho\chi$, for reduced temperatures up to $T_R = 2.0$ and reduced pressures up to $P_R = 15$ for both the gaseous and liquid states. This modulus can be applied to account for the effect of pressure on viscosity, thermal conductivity, and self-diffusivity. The value of this modulus at the critical point has been established from the PVT data to be $(b\rho\chi)_c = 0.784$ and is identical to the value resulting from the relationship $(b\rho\chi)_c = \alpha_c z_c - 1$. The resulting reduced state correlation should be applicable to substances having critical compressibility factors similar to ethane ($z_c = 0.285$).

PRESENT interest in the calculation of the transport properties of substances in their dense gaseous and liquid states has been expressed along the lines proposed by Enskog (*6*). The model considered by Enskog involved collisions between rigid spherical molecules. For this idealized system, the effect of pressure on viscosity, thermal conductivity, and self-diffusivity was:

$$\frac{\mu}{\mu^*} = b\rho\left[\frac{1}{b\rho\chi} + \frac{4}{5} + 0.7614\, b\rho\chi\right] \tag{1}$$

$$\frac{k}{k^*} = b\rho\left[\frac{1}{b\rho\chi} + \frac{6}{5} + 0.7574\, b\rho\chi\right] \tag{2}$$

$$\frac{(\rho\Delta)}{(\rho\Delta)} = \frac{b\rho}{b\rho\chi} \tag{3}$$

where $b = (2\pi\sigma^3/3m)$ for rigid spherical molecules and χ is a correction factor accounting for the probability of collisions. These relationships require that $b\rho\chi$, the Enskog modulus, be known at the conditions of temperature and pressure for which the transport properties of the substance are desired. The Enskog modulus is defined by the equation of state:

$$P + a\rho^2 = \frac{RT}{M}\left[1 + b\rho\chi\right] \tag{4}$$

from which the following relationship results with the assumption that a and b are constant:

$$b\rho\chi = \frac{M\rho}{R}\left(\frac{\partial P}{\partial T}\right)_\rho - 1 \tag{5}$$

Equation 5 can be expressed in terms of reduced variables to give:

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

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