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Determination of the Thermal Conductivity of Argon and Nitrogen over a Wide Temperature Range Through Data Evaluation and Shock-Tube Experiments[1]

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Reliable and well-established methods to measure the thermal conductivity of gases are available only in the moderate temperature range, namely, up to about 1000 K. In the present study, a set of the most probable thermal conductivity values of components of gaseous combustion products in a wide range of temperatures has been obtained through an optimum combination of three procedures: critical assessment of available data in the moderate temperature range, experimental determination by the shock-tube method at high temperatures, and theoretacal estimation of temperature dependence in the intermediate temperature range. Among the components of combustion products, one monatomic gas and one diatomic gas, namely, argon and nitrogen, were studied in the present paper. The shock-tube measurements have been performed in the temperature ranges 1000–4500 K for argon and 500–2200 K for nitrogen. The results of the critical evaluation and the shock-tube measurements have been combined with the aid of theoretically assumed temperature dependence of the thermal conductivity.

KEY WORDS: argon; data evaluation; high temperature; nitrogen; shock-tube measurement; thermal conductivity.

1. INTRODUCTION

The condition of gases used for high-temperature gas turbines or MHD power plants has continually been raised in order to attain a higher ther-

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mal efficiency. This presupposes the availability of reliable thermophysical property data for working fluids and materials. The present study is a part of the program to obtain a consistent set of thermophysical property data for component gases and typical mixtures in high-temperature combustion products. Among various thermophysical properties, transport property data are quite scarce at high temperatures, and considerable effort to study these properties is demanded. However, conventional methods for measuring transport properties can normally give reasonably precise data only in the moderate temperature range, that is, up to about 1000 K. At higher temperatures, experimental determination is extremely difficult and the accuracy is poor even if the measurement is possible. Although theoretical estimation seems to be an alternative method, existing values obtained by various estimation theories diverge extensively at high temperatures. Since theories have proved to predict at least the temperature dependence reasonably well over a certain range of temperature, the accuracy of the theoretical estimates can be raised if a fixed point is given in the highest temperature range.

The present study was intended to determine thermal conductivities for gases through an optimum combination of three means: first, a critical evaluation of available experimental data at temperatures below 1000 K; second, measurements by the shock-tube method at high temperatures; and third, interpretation of the results of the above two methods with the aid of theoretically estimated temperature dependence. Among component gases of combustion products, argon and nitrogen are selected as the most important components as a monatomic and a diatomic gases.

2. TEMPERATURE DEPENDENCE OF GAS THERMAL CONDUCTIVITY

The thermal conductivity of a dilute monatomic gas can be expressed by Eucken's simple relation,

$$\lambda = \frac{5}{2}\eta c_v \tag{1}$$

where η is the viscosity and c_v is the isochoric specific heat ($c_v = 3R_0/2M$). R_0 is the gas constant and M is the molecular weight. Molecular theory of dilute gas predicts that the viscosity is approximately proportional to $\sqrt{T}$ at high temperatures, therefore a correction factor $f_1(T)$, defined by

$$\lambda = \sqrt{T} f_1(T) \tag{2}$$

can be represented by a simple power series of temperature T with a few terms.

In the case of polyatomic gases, we cannot neglect the contribution of the internal energy of the molecule to the thermal conductivity. Therefore, as shown by Hirschfelder *et al.* [1], the thermal conductivity is expressed as

$$\lambda = \eta \left\{ \frac{5}{2} c_{\mathrm{vtr}} + \frac{\rho D_{\mathrm{int}}}{\eta} c_{\mathrm{vint}} \right\} \tag{3}$$

where c_{vtr} is the contribution of translational energy $c_{\mathrm{vtr}} = 3R_0/2M$ and c_{vint} is that of internal energy. ρ is the density and D_{int} is the diffusion coefficient for internal energy. The product $\rho D_{\mathrm{int}}/\eta$ is almost independent of temperature and, according to molecular theories, is close to 1.33 for most gases. Since the contribution of inelastic collisions is not accounted for in Eq. (3), we have further to apply another correction factor $f_2(T)$, which is slightly smaller than unity and a weak function of temperature. Therefore the equation can be rewritten as

$$\lambda = f_2(T)\, \eta \left\{ \frac{15R_0}{4M} + 1.33 c_{\mathrm{vint}} \right\} \tag{4}$$

For nitrogen at temperatures up to 2200 K, c_{vint} changes also as a comparatively weak function of temperature. The product $f_1(T)\, f_2(T)$ has a comparatively weak temperature dependence. Thus the temperature of the thermal conductivity of nitrogen can also be expressed by a simple polynomial of temperature,

$$\lambda = \sqrt{T} \sum k_i T^i \tag{5}$$

3. SELECTION OF AVAILABLE DATA AT MODERATE TEMPERATURES

3.1. Argon

For the thermal conductivity of argon, a literature survey was carried out [2]. Data published before 1960 were disregarded, since experimental data on thermal conductivity published before 1960 show considerable disagreement with each other in the case of most fluids. Also, the progress of experimental technique since then was so great, this selection could be justified. Fifty-three reports published after 1960 have been found and examined. Considering such items as the reliability of measuring principles, description of apparatus, considerations on various corrections, precision claimed by the authors, reproducibility of measured data, and so on, several sets of data were selected as the basis for a preliminary correlation covering the temperature range of up to 1000 K. The selected data are those of Vargaftik and Zimina [4], Le Neindre [10], Haarman [11], Kestin *et al.* [14], Assael and Wakeham [16], and Haran *et al.* [18]. They, with other studies [3–18], are listed in Table I. Values calculated by this preliminary equation were used in optimum fitting for the entire range of temperature, as described in the next section.

3.2. Nitrogen

Many experimental data of the thermal conductivity of nitrogen are available. With the studies published before 1960 disregarded, 41 reports have been examined, and those listed in Table II were selected for further consideration [3, 5, 9–11, 15, 17–25]. Among them, high credit was given to works by Le Neindre [10], Haarman [11], Clifford *et al.* [15], Vargaftik and Zimina [20], Assael and Wakeham [24], and Imaishi *et al.* [25]. They were used as the basis for a preliminary correlation. Other procedures were similar to those for argon.

Table I. Experimental Studies of the Thermal Conductivity of Argon (After 1960, Above 300 K)

Author(s)	Year	Method[a]	Temperature (K)	Claimed accuracy (%)	Ref. No.
Schramm	1964	1	276–1394	±2–3	3
Vargaftik and Zimina	1964	2	311–1201		4
Keyes and Vines	1965	3	413– 620		5
Correia *et al.*	1968	1	276–1251	±1	6
Gray and Maczek	1968	1	323– 373	±2	7
Saxena and Saxena	1968	2	373–1473	±2	8
Faubert and Springer	1972	2	800–2000	±2.5–4	9
Le Neindre	1972	3	298– 977	±2.5	10
Haarman	1973	4	328– 468	±0.3	11
Springer and Wingeier	1973	2	1000–2500	±2–4	12
Chen and Saxena	1975	2	350–2500	±1.5	13
Kestin *et al.*	1980	4	301	±0.3	14
Clifford *et al.*	1981	4	313– 375		15
Assael and Wakeham	1982	4	308	±0.2	16
Yorizane *et al.*	1983	3	298– 324	±3	17
Haran *et al.*	1983	4	308– 429	±0.3	18

[a] (1) Hot wire (steady state); (2) hot wire (steady state, thermal diffusion column); (3) concentric cylinders; (4) hot wire (transient).

Table II. Experimental Studies of the Thermal Conductivity of Nitrogen (After 1960, Above 300 K)

Author(s)	Year	Method[a]	Temperature (K)	Claimed accuracy (%)	Ref. No.
Westenberg and deHaas	1962	5	300–1000		19
Schramm	1964	1	276–1394	±2–3	3
Vargaftik and Zimina	1964	2	304–1134		20
Keyes and Vines	1965	3	273– 773		5
Faubert and Springer	1972	2	800–2000	±2.5–4	9
Le Neindre	1972	3	301– 801	±2.5	10
Chen and Saxena	1973	2	373–2473	±1.5	21
Haarman	1973	4	328– 468	±0.3	11
Saxena and Chen	1975	2	338–2518	±1.5	22
Clifford *et al.*	1979	4	301		23
Assael and Wakeham	1981	4	308	±0.2	24
Clifford *et al.*	1981	4	345– 388		15
Yorizane *et al.*	1983	3	299– 323	±3	17
Haran *et al.*	1983	4	308– 429	±0.3	18
Imaishi *et al.*	1984	4	301		25

[a] (1) Hot wire (steady state); (2) hot wire (steady state, thermal diffusion column); (3) concentric cylinders; (4) hot wire (transient); (5) line source.

4. EXPERIMENTAL DETERMINATION BY THE SHOCK-TUBE METHOD AT HIGH TEMPERATURES

4.1. Principle and Procedure

At high temperatures, measurement of the thermal conductivity by the shock-tube method was carried out. The method is considered to be the only method which is practically applicable to a high-temperature gas. Since first used by Smiley in 1957 [26], many studies by this method have been published and a number of improvements have been proposed [27]. The principle of the method employed in the present study is similar to that used by Mastovsky and Slepicka [28, 29]. After a shock wave is generated in a shock tube and reflected by the end wall, the sample gas near the wall is heated by compression from initial temperature T_1 to temperature T_5 (Fig. 1). The pressure is also raised from P_1 to P_5. The sample gas is kept at temperature T_5 for a period of 0.5 to 1.5 ms. The end wall is

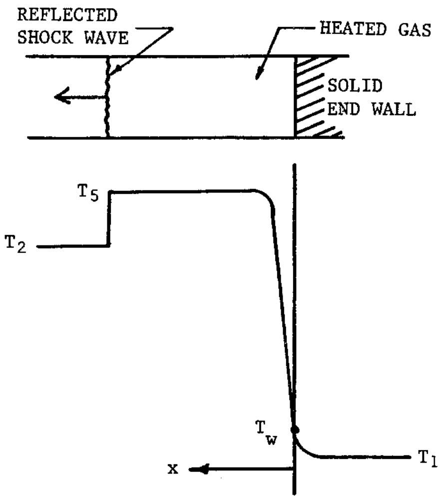


Fig. 1. Sketch of the temperature profile at the wall.

heated by heat conduction from the gas. The temperature rise in the wall is expressed by the equation

$$\frac{\partial T}{\partial t} = a_s \frac{\partial^2 T}{\partial x^2} \tag{6}$$

where T is the temperature, t is the time, a_s is the thermal diffusivity, and x is the distance. The subscript s means wall material. The temperature of the gas at the surface of the wall T_w is expected to be not far from the initial uniform temperature T_1, and the thermal diffusivity a_s is assumed to be constant. For the gas, the energy equation is given as

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\lambda \frac{\partial T}{\partial x}\right) \tag{7}$$

where ρ is the density, c_p is the specific heat, and λ is the thermal conductivity of the gas. Convection and radiation in the gas are neglected since the measurement is completed in a very short time and the gases considered are nonradiative at the test temperatures. The pressure of the gas is so low that it can be treated as the ideal gas. The continuity of temperature at the wall was assumed.

An initial condition and the boundary conditions are as follows.

$T = T_1$ at $t = 0$

$T = T_w$ at $x = 0$ and $t = \infty$

$T = T_1$ at $x = -\infty$

$T = T_5$ at $x \gg \delta$ (δ, thickness of the boundary layer)

$$\lambda_s \left(\frac{\partial T}{\partial x}\right) = \lambda_w \left(\frac{\partial T}{\partial x}\right) \quad \text{at } x = 0$$

Also, assuming constant properties for the solid wall, the following equation can be obtained [28]:

$$\lambda = \frac{\lambda_s \rho_s c_s}{(\rho c_p)_{P_5}} \left\{ \left[\frac{\partial (T_w - T_1)}{\partial T_5} \right]_{P_5} \right\}^2 \tag{8}$$

The rise of the surface temperature, $T_w - T_1$, can be measured using, for example, a thin platinum film as a resistance thermometer and can be expressed as

$$T_w - T_1 = \frac{1}{\alpha} \frac{\Delta E}{E} \tag{9}$$

where α is a calibration constant and ΔE is the potential drop. From Eqs. (8) and (9), and assuming the ideal-gas state, the thermal conductivity of the gas can finally be obtained with the following equation:

$$\lambda = \frac{\lambda_s \rho_s c_s}{\alpha (\rho c_p)_P} \left\{ \frac{d[\Delta E \sqrt{P} / (E \sqrt{P_5})]}{dT_5} \right\}^2 = \frac{k_w}{(\rho c_p)_P} \left(\frac{\partial F}{\partial T_5} \right)^2 \tag{10}$$

where k_w is an apparatus constant. The derivative dF/dT_5 can be calculated from the relation between F and T_5, which is determined experimentally by repeating measurements of temperature and pressure of the shock-heated gas and of the temperature rise at the wall surface.

In the present study, the form of the function F is assumed as

$$F = \frac{k_1}{T} + k_2 + k_3 T^{0.5} + k_4 T^{0.75} + k_5 T \tag{11}$$

based on considerations in Section 2. The function F was determined by fitting Eq. (11) to experimentally obtained values of F at high temperatures and, at the same time, to F values calculated from thermal conductivity data at lower temperatures. These lower-temperature data were determined through critical evaluation as described in the previous section. In the actual procedures, the derivatives

$$\frac{dF}{dT}=\sqrt{\frac{\lambda}{k_w}\rho c_p} \tag{12}$$

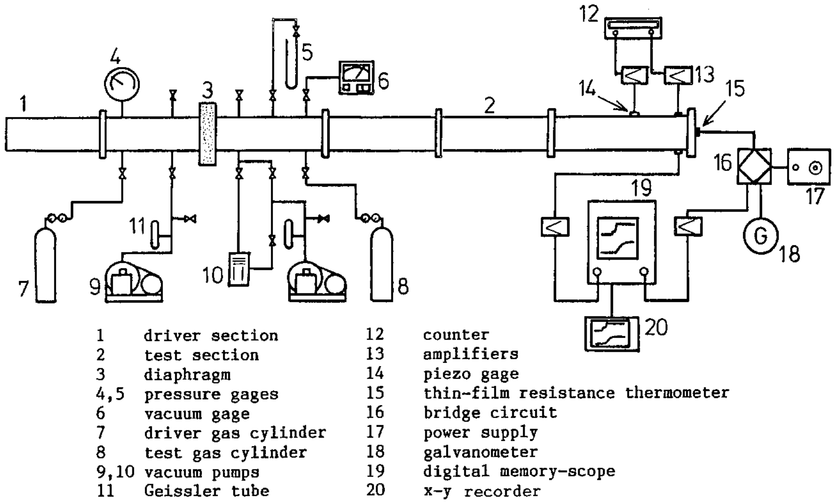
were calculated from the evaluated data set. Considering that $F=0$ at $T=T_1$ ($T_1=300$ K in the present study), Eq. (12) was integrated to obtain F. The thermal conductivity was calculated by Eq. (10) using the final form of function F.

For argon, temperature T_5 was calculated from the shock speed U as

$$T_5=\frac{[2(\kappa-1)M_s^2+(3-\kappa)][(3\kappa-1)M_s^2-2(\kappa-1)]}{(\kappa+1)^2M_s^2}T_1 \tag{13}$$

where κ is the ratio of the specific heats, 1.667 for argon, and M_s is the Mach number:

$$M_s=\frac{U}{\sqrt{\kappa R_0 T_1}} \tag{14}$$



1	driver section	12	counter
2	test section	13	amplifiers
3	diaphragm	14	piezo gage
4,5	pressure gages	15	thin-film resistance thermometer
6	vacuum gage	16	bridge circuit
7	driver gas cylinder	17	power supply
8	test gas cylinder	18	galvanometer
9,10	vacuum pumps	19	digital memory-scope
11	Geissler tube	20	x-y recorder

Fig. 2. Schematic diagram of the experimental setup.

And for nitrogen, T_5 was calculated with the following relation:

$$T_5 = [(h_5 - h_2) - u_2^2/2] \left[\frac{T_2}{(h_5 - h_2) + u_2^2/2} \frac{1}{R_0} \right] \tag{15}$$

where u_2 and h_2 are the speed and the enthalpy of the gas behind the shock, respectively.

4.2. Apparatus

The schematic diagram of the experimental setup is shown in Fig. 2. The inner diameter of the shock tube was 76.2 mm. The lengths of the driver and driven tubes were 3 and 6 m, respectively. The driver gas was helium, whose pressure was 0.2–1.0 MPa. The pressure of the driven gases, argon and nitrogen, was 1.0–10 kPa. Two pressure sensors were fixed with the interval of 0.5 m and used for the measurement of the shock speed. The third pressure sensor was used for the pressure measurement. Pressure sensors were connected to a digital memory scope. The temperature variation of the wall surface was measured as the change in the resistance of a thin platinum deposited on one end of a pyrex glass rod 12 mm in diameter. The temperature sensor is shown in Fig. 3. The width of the film strip was about 1 mm. The total resistance was 120 to 130 Ω for different sensors. The change of the resistance was detected as unbalanced voltage and recorded in a digital memory scope. Records in the digital memory scope were drawn on a X–Y recorder. The sensor was calibrated with a standard thermometer. Measurements were performed for a monatomic gas, argon, in the temperature range 1038–4336 K and a diatomic gas, nitrogen, in the temperature range 590–2224 K.

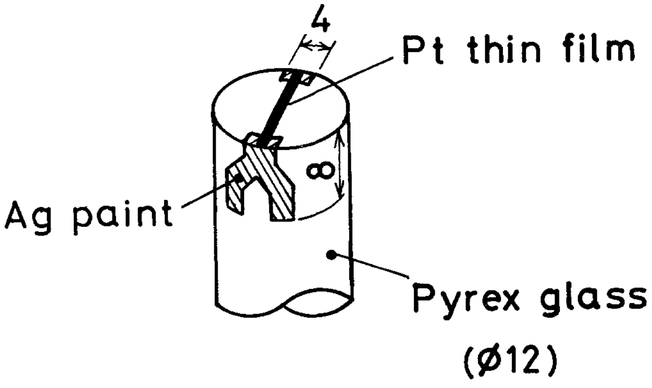


Fig. 3. Sensor for temperature measurement.

5. RESULTS

5.1. Thermal Conductivity of Argon

Measurement of argon was carried out for temperatures up to 4336 K, and 37 experimental points were obtained. The purity of the sample gas was 99.99%. The function F and measured data are shown in Fig. 4. Reproducibility can be seen in the deviation plot in Fig. 5. The specific heat was obtained from Ref. 30. The enthalpy was calculated from the specific heat.

The new equation of the thermal conductivity of argon was determined as

$$\lambda = \sqrt{T}\left(\frac{a_1}{T} + a_2 + a_3 T\right) \tag{16}$$

where

$$a_1 = -1.125 \times 10^2$$

$$a_2 = 1.354 \times 10^0$$

$$a_3 = 1.453 \times 10^{-4}$$

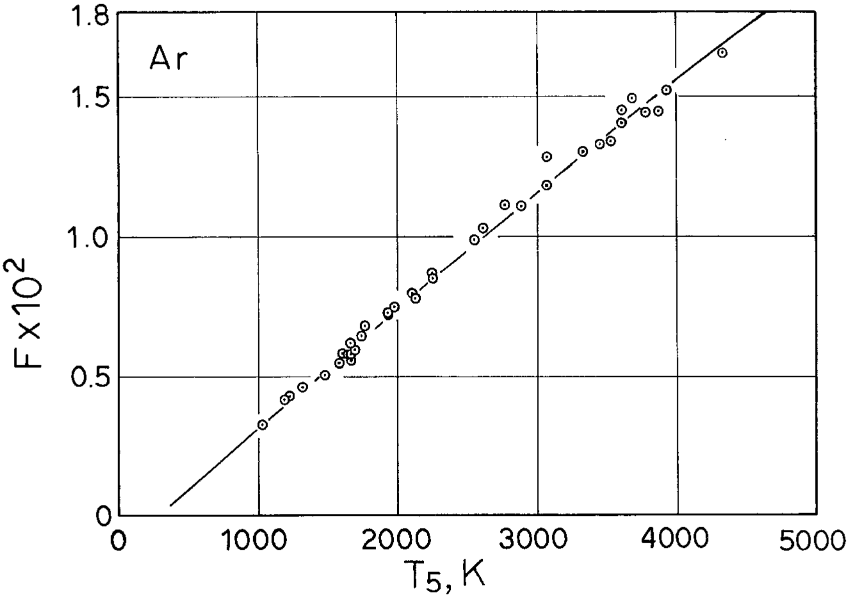


Fig. 4. Function F and measured data for argon.

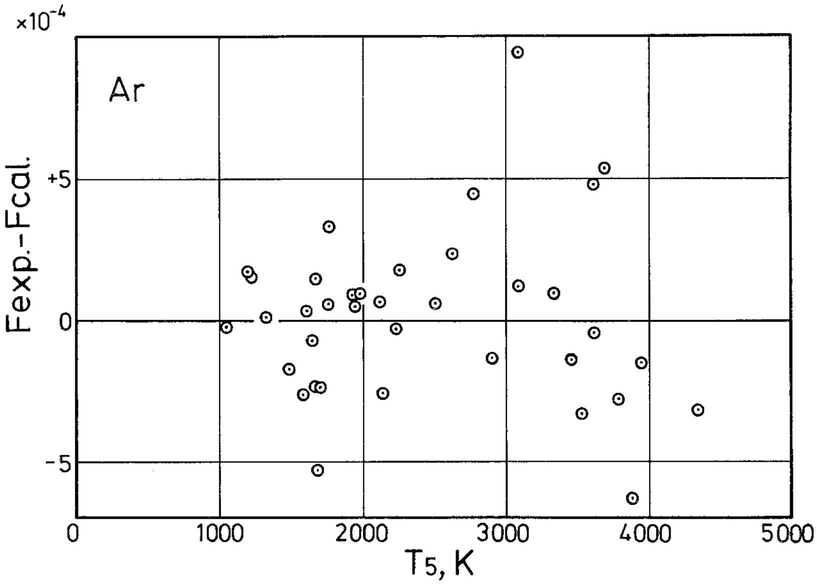


Fig. 5. Deviations of measured data from function *F* (argon).

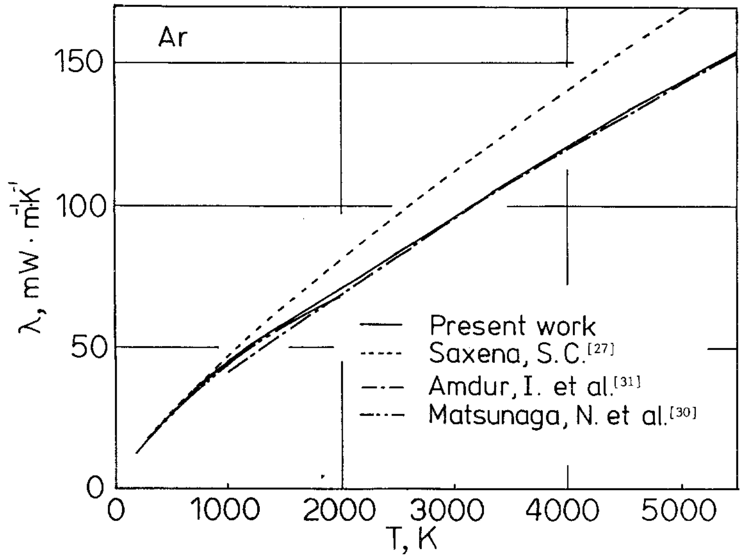


Fig. 6. Thermal conductivity of argon at high temperatures.

and λ is in $\mathrm{mW\,m^{-1}\,K^{-1}}$ and T is in K. The range of validity is 300–4500 K and the estimated reliability is about 3% below 1000 K and 9% at the highest temperature. Equation (16) is compared with previous studies in Fig. 6. Values in Ref. 30 were values extrapolated from evaluated experimental data at temperatures below 1000 K. Agreement between these studies is reasonably good for argon. The present results give values lower by about 10% than data by Saxena [27]. Better agreement was obtained with theoretical prediction by Amdur and Mason [31]. Comparisons at lower temperatures are shown in Fig. 7.

5.2. Thermal Conductivity of Nitrogen

In the case of nitrogen, there is possibility of dissociation. The equilibrium constant of thermal dissociation K_p for nitrogen was taken from JANAF thermochemical tables [32]. A simple equation representing these values was correlated as

$$\log K_p = b_0 + b_1(1000/T) + b_2(1000/T)^2 \tag{17}$$

where K_p is in atm and constants are

$$b_0 = 0.3528 \times 10^1$$

$$b_1 = -0.2515 \times 10^2$$

$$b_2 = 0.9516 \times 10^{-1}$$

The molecular weight, the enthalpy, and the specific heat were corrected for dissociation. Even at the highest temperature in the present study, the effect of dissociation is not much, since the mole fraction of N is estimated as 0.06% at 2500 K. The purity of nitrogen used was 99.99%. The function F for nitrogen is shown in Fig. 8 and the deviation plot is given in Fig. 9.

Thermal conductivity of nitrogen in the temperature range 300–2200 K is expressed by

$$\lambda = \sqrt{T}\left(\frac{c_1}{T} + c_2 + c_3 T\right)$$
$$c_1 = -9.239 \times 10^1, \qquad c_2 = 1.647 \times 10^0, \qquad c_3 = 5.255 \times 10^{-4} \tag{18}$$

The estimated uncertainty is 1% at 300 K and about 8% at 2200 K.

The present results are compared with previous works as shown in Fig. 10. The present results agree very well with the authors' previous prediction [30]. The deviation from Saxena's value [27] is larger than that

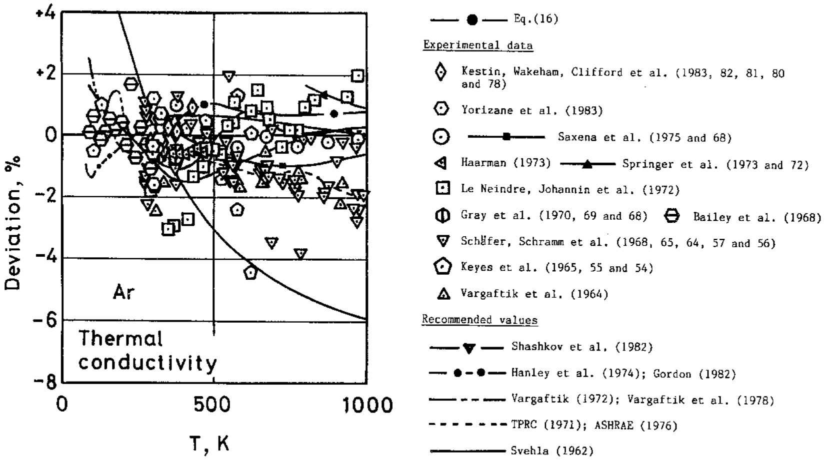


Fig. 7. Comparisons of the thermal conductivity of argon at temperatures up to 1000 K.

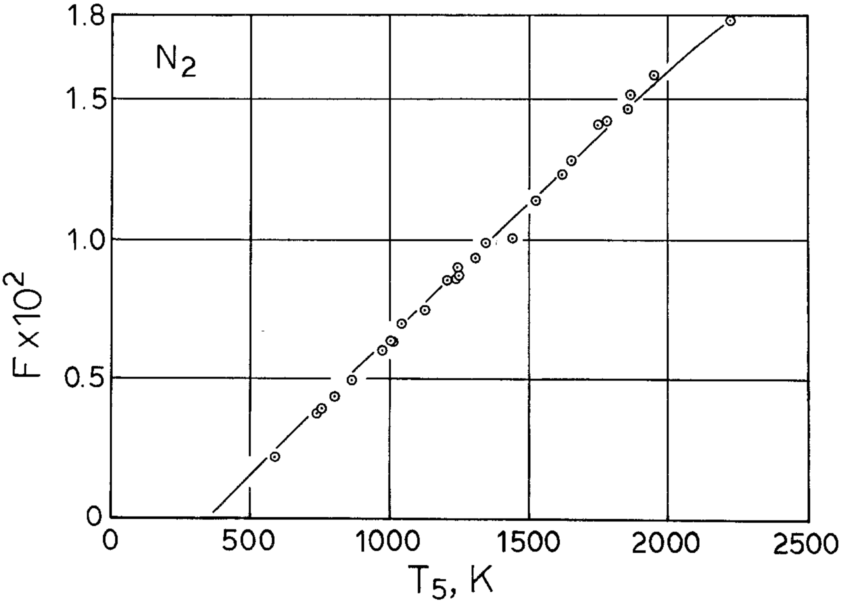


Fig. 8. Function *F* and measured data for nitrogen.

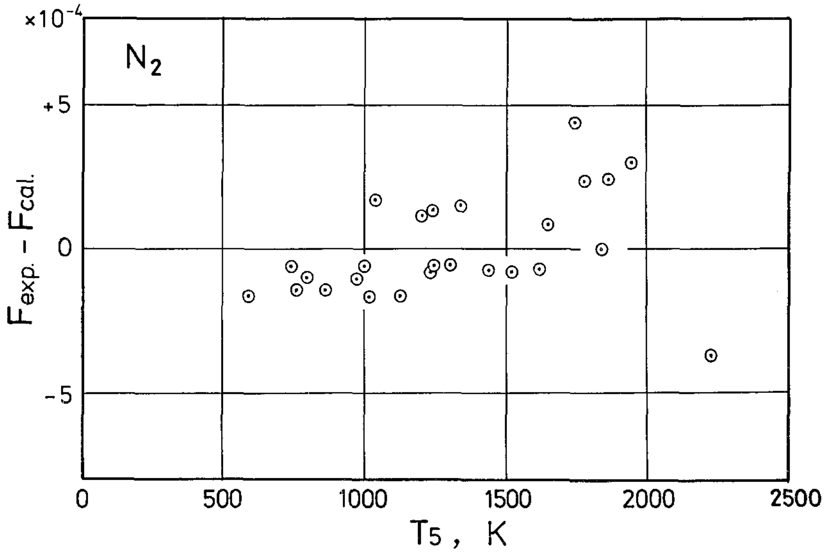


Fig. 9. Deviations of measured data from function *F* (nitrogen).

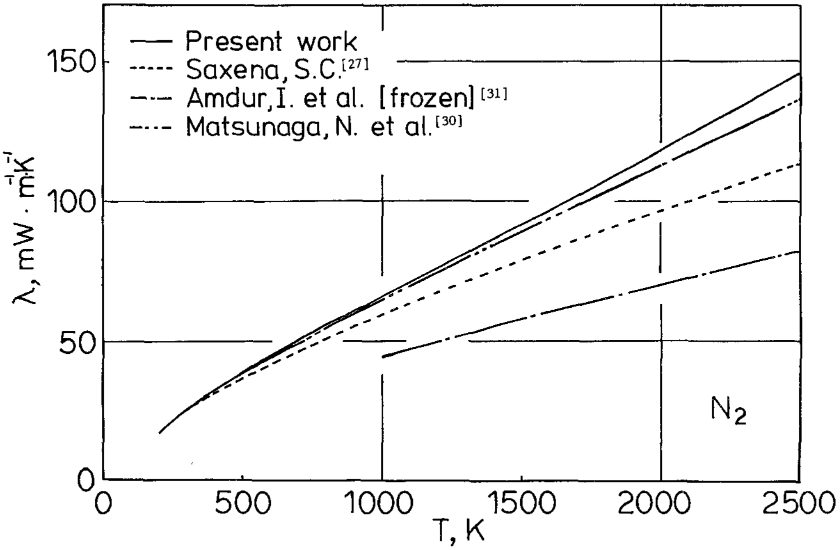


Fig. 10. Thermal conductivity of nitrogen at high temperatures.

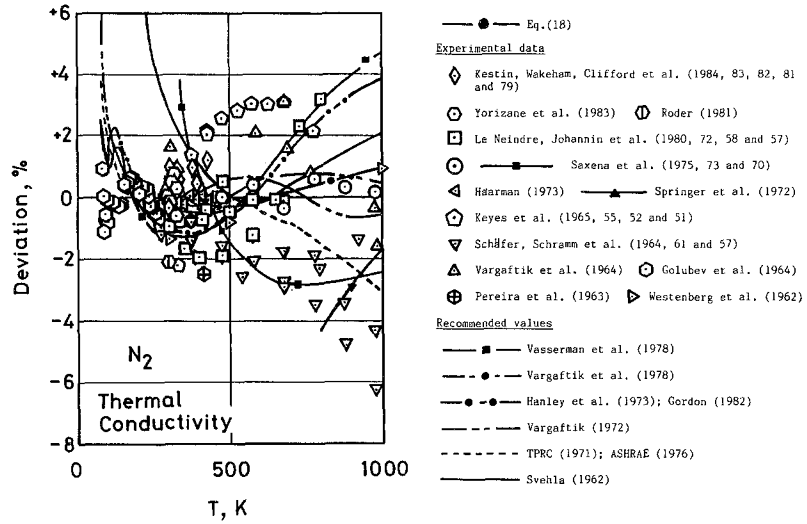


Fig. 11. Comparisons of the thermal conductivity of nitrogen at temperatures up to 1000 K.

for argon. Comparisons of other experimental data at lower temperatures with Eq. (18) are shown in Fig. 11. It is found that Eq. (18) represents the thermal conductivity of nitrogen reasonably well also at lower temperatures.

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