

Measurement of Transport Properties of High-Temperature Fluids

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Received January 2, 1990

High-temperature fluids often show interesting behavior and have important industrial applications, however, their thermophysical properties are extremely difficult to measure. Sometimes there are no measuring methods available, despite the fact that the great industrial demand for data on these property data at high temperatures is intense in recent years. In the present paper, five examples of approaches to measure transport properties of high temperature fluids are described. They include measurements of the viscosity of high-temperature melts by the oscillating-cup method, of the viscosity of vapors of H₂O and D₂O by the capillary method, of the thermal conductivity of molten salts by the transient hot-wire method, and of the thermal diffusivity by the optical method and of the thermal conductivity of high temperature gases by the shock-tube method.

KEY WORDS: alkali metals; high temperature; molten salts; thermal conductivity; thermal diffusivity; viscosity.

1. INTRODUCTION

High-temperature fluids have always been fascinating targets of ambitious experimentalists, since these substances show scientifically interesting behavior, are important in industrial applications, and are often very difficult to measure. Measurements of transport properties pose special challenges. Except, for example, for dilute gases of simple molecules, quantitative theoretical predictions are not available. Sometimes a measuring method is not known. Application of conventional methods which are well established at moderate temperatures requires complicated precautions at high temperatures. Indispensable requisites for reliable experimental

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measurement of transport properties are correct working equations, properly controlled fluid conditions, and experimental skill.

Interesting high-temperature fluid systems in recent years and in the near-future are (1) high-temperature reactive or corrosive liquids, (2) gases and liquids at high temperatures and high pressures, (3) high-temperature melts, (4) gaseous or liquid mixtures at high temperatures, and (5) dissociated or ionized gases [1]. Difficulties vary for different fluids and a general rule is not adequate for reliable measurements.

Presently, in this paper, five examples of investigating these high-temperature fluids are described, taken from studies performed in our laboratory. Two attempts for measuring the viscosity and three attempts for measuring the thermal conductivity of high-temperature fluids are described.

2. VISCOSITY OF HIGH-TEMPERATURE MELTS

In recent years, melts of certain inorganic materials have become increasingly important in advanced technologies. They include molten salts, molten metals, and molten semiconductor materials, all of which are increasingly reactive or corrosive at high temperatures.

For measuring the viscosity of high-temperature melts, which have relatively low viscosities, two major types of experimental methods are generally applicable, namely, the capillary method and the oscillation method. While the capillary method has been used mostly as a relative method in a number of studies on high-temperature melts, difficulties due to the corrosion and the capillary machining cause the highest applicable temperature of this method to be limited to 1300–1600 K.

The oscillation method is more suitable since it can be applied in two different variations. One method has a suspended pendulum, generally a disk, cylinder, or sphere, immersed in the fluid to be investigated and the other method has the fluid contained in a suspended spherical or cylindrical hollow crucible. This so-called oscillating-cup viscometer consists essentially of an oscillating system with a thin suspension wire and a hollow cylindrical cup which contains the fluid. Once a torsional oscillation is started in the system, it follows a damped oscillation with a constant period and a constant decrement. The viscosity can be evaluated from these observed parameters [2–6].

The following features suggest that the oscillating-cup method is the most suitable one for measuring the viscosity of high-temperature melts. Only a small amount of specimen is required for measurements. The desired temperature condition can easily be attained since the specimen is

contained in a small cup. Suitable material for the cup can be found even for corrosive fluids, and its cylindrical shape allows precise machining.

In contrast to the inherent advantages of the oscillating-cup method over others, its mathematical complexity has limited its extensive application. Most of the earlier measurements, therefore, were performed on a relative base. Then Kestin and Newell [7] derived a solution by introducing the Laplace transform so as to facilitate the evaluation.

The main part of the apparatus used in our laboratory is shown in Fig. 1. The oscillating system, which consists of a Pt92-W8 suspension wire 11 of 0.2-mm diameter (2), a reflection mirror with its holder (3), an inertial disk (4), a molybdenum connecting rod (5), and a cylindrical cup (6), is suspended in a closed vessel. The vessel can be evacuated to $\sim 10^{-4}$ Pa, so that errors during the run due to any remaining gas can be eliminated.

The specimen in the cup is heated with an electric furnace which has 14 heating elements made of SiC, and the temperature of the cup can ultimately reach 1800 K. In any kind of oscillation viscometry, the

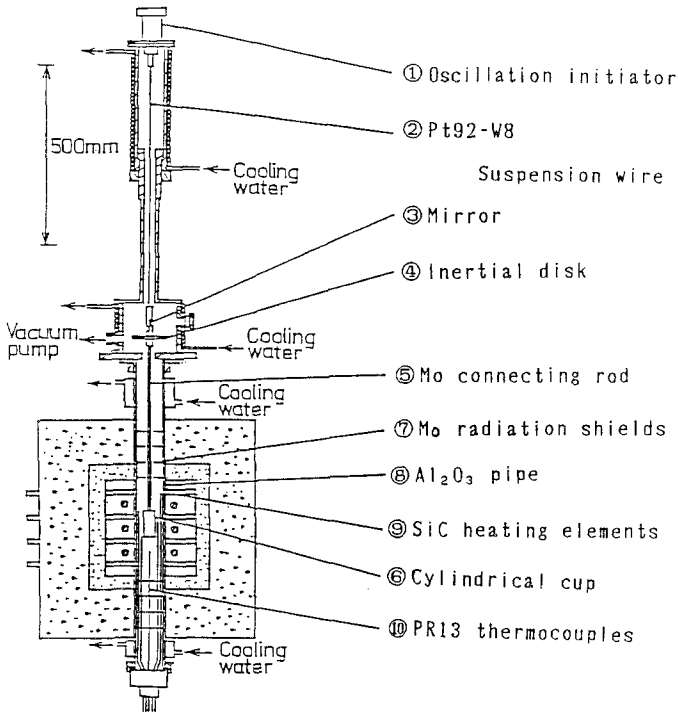


Fig. 1. Oscillating-cup viscometer.

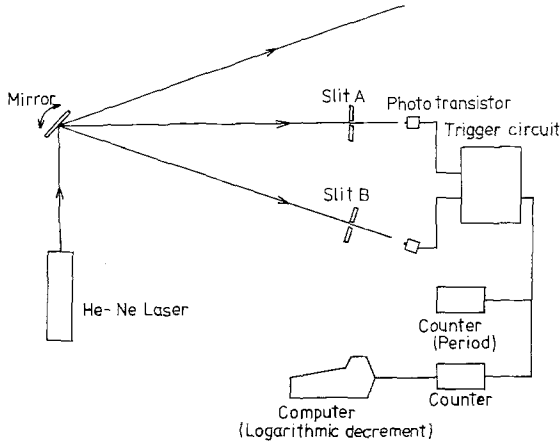


Fig. 2. Optical system of the oscillating-cup viscometer.

experimental error is governed in large part by an uncertainty in the measurement of the decrement. The measurements of the period and the logarithmic decrement were carried out with the aid of the optical measuring system shown in Fig. 2.

As an example, Fig. 3 shows results for the viscosity of NaCl [5]. These results give an illustration of the applicability of the method over a very wide temperature range.

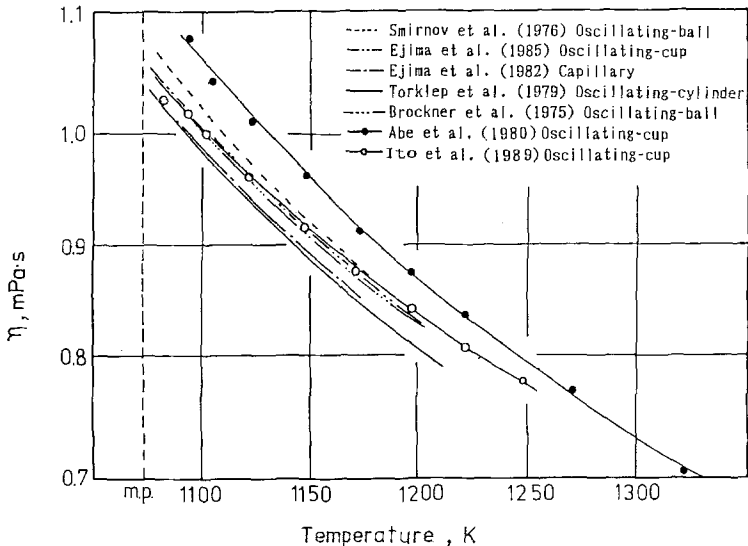


Fig. 3. Viscosity of sodium chloride. References: 3, 4, 37-39, 41.

Measurements of the viscosity of molten lithium [6] showed that some earlier measurements were too low due to the use of an incorrect working equation and to the chemical reaction of the specimen with the cup wall. Such a chemical reaction with the cup wall caused a decrease in the viscosity of lithium when the cup material had been changed from TZM alloy to molybdenum [6].

3. VISCOSITY OF FLUIDS AT HIGH TEMPERATURES AND HIGH PRESSURES

The viscosity of gaseous D_2O , or deuterium oxide, shows a negative pressure effect in the temperature range 200–500°C, while D_2O shows a positive pressure dependence in the liquid, or in dense gas, at high pressures. Information about the behavior of D_2O in the intermediate region not only is interesting from a scientific point of view, but also is necessary to formulate accurate correlating equations for various engineering purposes. When data on D_2O under high pressures is needed in various applications including nuclear power engineering, the practical way presently available is estimating it from data on H_2O with the aid of corresponding states. Experimental data will be useful also for testing the limit of many corresponding-states calculations [8, 9].

Since, not only the temperature, but also the pressure range is large, the capillary method is preferable. An experimental setup is shown in Fig. 4

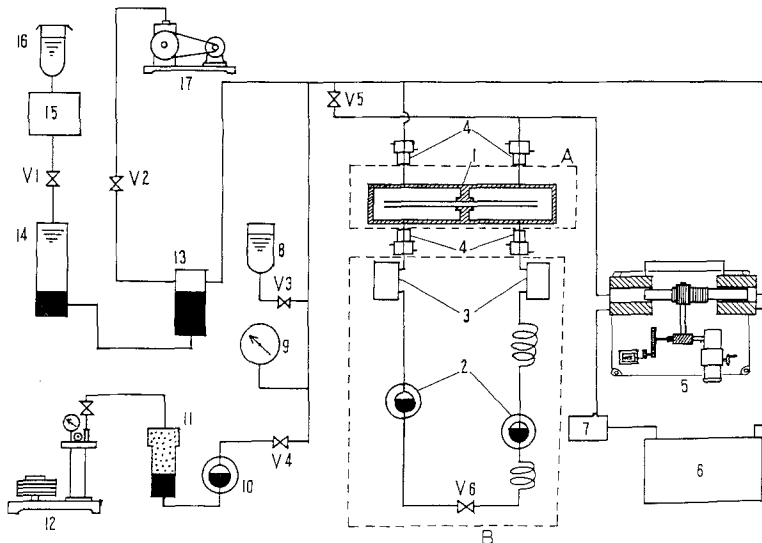


Fig. 4. Closed-circuit capillary viscometer for high-pressure fluids.

[10]. The method is closed-circuit transpiration method. The capillary, made of platinum-rhodium alloy, has a length of 500 mm and an inner diameter of 0.32 mm. The test fluid flows from one side of the high-pressure injector (5) and returns to the other side of the injector after flowing through the capillary (1).

The pressure drop over the length of the capillary is measured with a mercury manometer which consists of two high-pressure windows (2), mercury traps (3), a valve (6), and a cathetometer. The injector (5) for constant flow rate has a plunger and two cylinders, and its temperature is controlled by circulating water from thermostat (6) by pump (7). The flow rate is measured from the revolution speed of a driving gear. The viscosity is determined with the aid of the Hagen-Poiseuille equation. Figure 5 shows our data as well as those of Rivkin et al. [11] for D_2O in the liquid and dense-gas region. The region investigated includes the critical region. Although the critical enhancement very close to the critical point has not been resolved accurately, the dramatic change in the viscosity is measured from negative pressure dependence in the vapor region at lower pressures

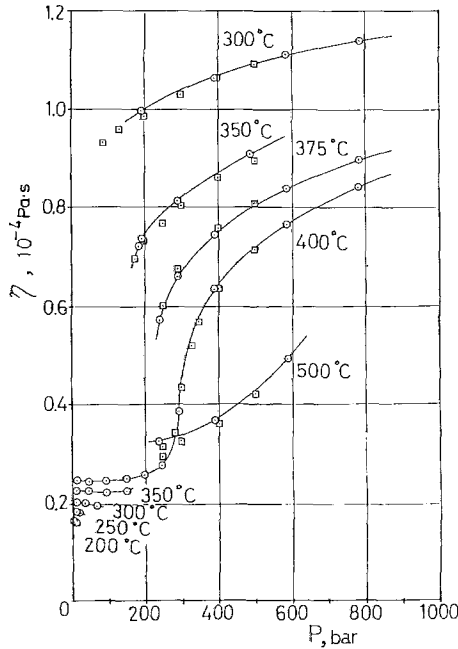


Fig. 5. The viscosity of D_2O . Circles, Abe et al. [10]; squares, Rivkin et al. [11].

to positive dependence in the liquid or dense gas region at high pressures [10, 12].

The trouble with the transpiration method is that the measured quantity is the kinematic viscosity. In order to get the viscosity, we need the density at high temperatures and high pressures. This is not easy, especially for mixtures or for fluids in the critical region. Another important point to be considered is the possible deviation of the flow pattern from the laminar condition due to the very low kinematic viscosity in the critical region.

Modified versions of the instrument have been used for a variety of substances such as seawater, fluorinated hydrocarbons, and other energy related fluids [13, 14].

4. THERMAL CONDUCTIVITY OF HIGH-TEMPERATURE MELTS BY THE TRANSIENT HOT-WIRE METHOD

Among various thermophysical properties, thermal conductivity is one of the most difficult properties to measure. The transient hot-wire method has been established as the most precise method for ordinary fluids and is capable of convection-free measurement except close to the critical point [15]. Convection poses a serious difficulty, especially for high-temperature fluids. In the case of the transient hot-wire method, which we have used for many fluids, a thin metallic wire is vertically supported in the fluid layer. After a step change in voltage applied to the wire starting at time $t = 0$, the temperature rise of the wire is related to the amount of heat conducted through the fluid layer.

Assuming that the radius of the wire is thin and the thickness of the fluid layer is great enough, and so on, the heat conduction equation and the thermal conductivity can be calculated from the ratio $\Delta T / \ln t$, where t is the time. The temperature rise of the wire ΔT can be measured by monitoring the resistance of the wire in a double-bridge circuit. Thus a plot of ΔT vs $\ln t$ should be a straight line and the slope of this line is inversely proportional to the thermal conductivity λ . In reality, the linear relation is observed for a limited period of time; and systematic deviations occur at small values of t due to the finite radius of the wire and, also, at large values of t due to convection or the finite thickness of the fluid layer.

The principle and special features of the transient hot-wire method were reported in detail in our earlier papers [16–19]. The most important point of this method is that it can eliminate error due to convection. This feature is especially attractive for measuring high-temperature fluids.

Unfortunately, molten salts are electrical conductors, and this prevents the application of a conventional transient hot-wire method for salts. In

earlier studies, coating or sheathing of the wire was unsuccessfully tested at high temperatures. The reason for the failure was due to the differences in the thermal expansion coefficients of the wire and coating material. In the study by Omotani et al. [20, 21], a new improved method was introduced: the thin metallic wire of a conventional hot-wire apparatus was replaced by a quartz glass capillary which contains mercury. Cracking of the coating layer due to a difference in thermal expansion or solid surface contact resistance between sheath and wire will not occur with this probe.

Thermal conductivity of the KNO_3 - NaNO_3 mixtures over the entire composition range was measured in the past by Bloom et al. [22] and by McDonald and Davis [23]. Using a concentric cylindrical apparatus, Bloom et al. measured thermal conductivity in the range 597 to 691 K. McDonald and Davis measured thermal conductivity at each melting point up to 733 K. The data of Bloom et al. showed a nonlinear dependence on composition and had a minimum value at $x=0.6$, where x is the mole fraction of KNO_3 . On the other hand, the data of McDonald and Davis showed an almost linear dependence on composition.

The results on composition dependence are shown in Fig. 6. The results of the present author's group at 590 K showed an almost linear dependence of the thermal conductivity on the mole fraction. The gradient was very close to the value by McDonald and Davis [23], although their values seemed too high. The discrepancies are about 10%, which exceeded the estimated experimental uncertainty of the present study. The tendency of the results of Bloom et al. [22] is nonlinear and completely different from both the present study and that of McDonald and Davis.

Our recent efforts to measure the thermal conductivity of molten salts

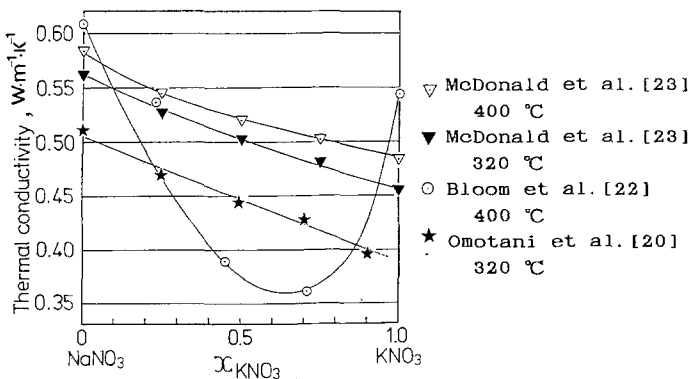


Fig. 6. Thermal conductivity of KNO_3 - NaNO_3 system.

by a wire probe coated with a thin layer of ceramics were also successful and the results have been reported in the literature [24]. Measurement of the thermal conductivity of an electrically conducting liquid is difficult.

5. THERMAL DIFFUSIVITY OF CORROSIVE AND ELECTRICALLY CONDUCTING FLUIDS BY AN OPTICAL METHOD

The best method to measure the thermal diffusivity of high-temperature fluids is undoubtedly a contact-free or remote-sensing method. An optical method has been developed by us. Although the principle of the method is not new, the method has been substantially improved by us and the new application to high-temperature melts has become possible [25–30].

The principle of the measurement is shown schematically in Fig. 7. A laser-beam pulse from a high-power laser is split into two beams of equal intensity by means of a beam splitter. The two beams cross a sample liquid at an angle θ and they cause an optical interference fringe pattern whose intensity distribution is spatially sinusoidal and equalizes to a uniform distribution with time. Being absorbed partially, this interference pattern gives a temperature grating in the sample liquid. If a grating period Λ is sufficiently small compared with the light absorption length α^{-1} , and if the grating period Λ is much smaller than the sample thickness d , we can consider this process of heat conduction as one-dimensional.

From the theory of heat conduction, we can get the relation among the thermal diffusivity a , the grating period Λ , and the time constant τ . Figure 8 shows the experimental apparatus. To confirm the reliability of

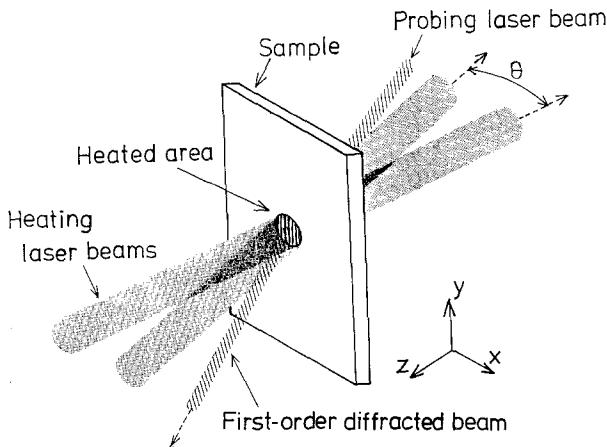


Fig. 7. Principle of the forced Rayleigh scattering method.

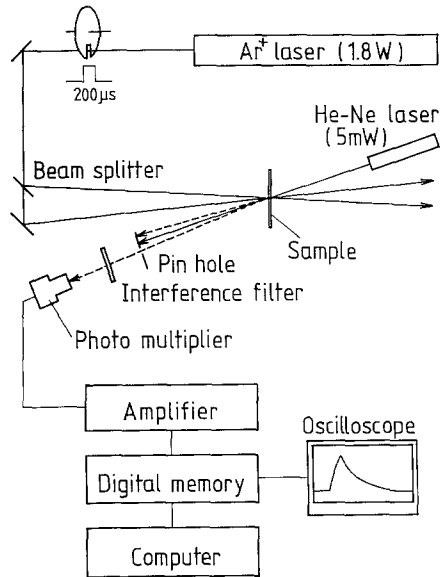
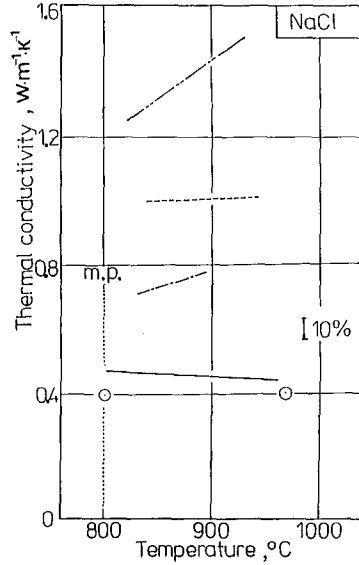


Fig. 8. Schematic diagram of thermal diffusivity apparatus by the forced Rayleigh scattering method.



---Bystrai et al. [42] ---Smirnov et al. [44]
 - - -Fedorov et al. [43] ○ Golyshev et al. [45]
 —Nakazawa et al. [48]

Fig. 9. Thermal conductivity of sodium chloride.

the method and the apparatus, checks were made by comparing our results on thermal diffusivity (converted to thermal conductivity) with values obtained by other methods. An example of the results is given in Fig. 9, which shows the thermal conductivity of sodium chloride. Earlier data from other research groups showed considerable disagreements. The present measurement gave the lowest values and the difference reached more than 300%. Furthermore, earlier data showed a strong positive dependence on temperature, while the new data show a very weak negative dependence. This is in accordance with our thermal conductivity data for other molten salts obtained with a modified transient hot-wire method.

6. THERMAL CONDUCTIVITY OF HIGH-TEMPERATURE GASES

The condition of gases used for high-temperature gas turbines or MHD power plants has continuously been raised in order to attain a higher thermal efficiency. This presupposes the availability of reliable thermophysical property data for working fluids and materials at temperatures up to several thousand degrees [31].

Almost the only method to measure the thermal conductivity of gases at temperature above 1500°C is the shock-tube method. The method was widely used in the 1960s but less in the 1970s. We considered the situation and came to the conclusion that the shock-tube method was worth another try, since sensors and electronic devices have improved greatly, and also the working equations have improved in the last decade.

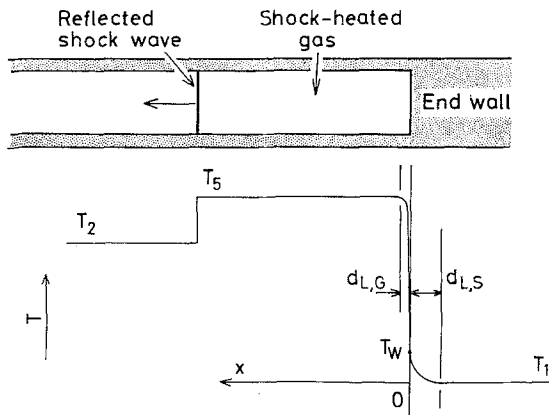


Fig. 10. Sketch of the temperature profile at the wall in a shock-tube experiment.

The study was intended to determine a consistent set of thermal conductivity data for a gas 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.

The principle of the method employed in the present study is similar to that used by Mastovsky and his co-workers [32, 33]. 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 an initial temperature T_1 to temperature T_5 as shown in Fig. 10. The pressure is also raised from P_1 to P_5 . The sample gas is kept at the temperature T_5 for a period of 0.5 to 1.5 ms. The end wall is heated by heat conduction from the gas. Assuming the ideal-gas state, the thermal conductivity of the gas can finally be obtained from repeated measurements of the temperature and pressure of the shock-heated gas and of the temperature rise at the end-wall surface.

The schematic diagram of the experimental setup is shown in Fig. 11. The inner diameter of the shock tube is 76.2 mm. Measurements on argon have been carried out for temperatures up to 4336 K [34, 35]. The results for the entire temperature range are shown in Fig. 12. From a critical evaluation of available data at lower temperatures and the shock-tube measurements at higher temperatures, the thermal conductivity of argon

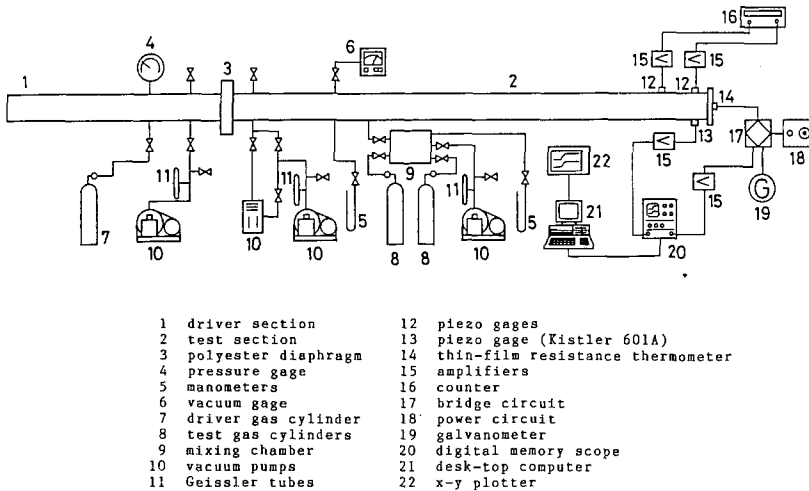


Fig. 11. Schematic diagram of the shock-tube apparatus.

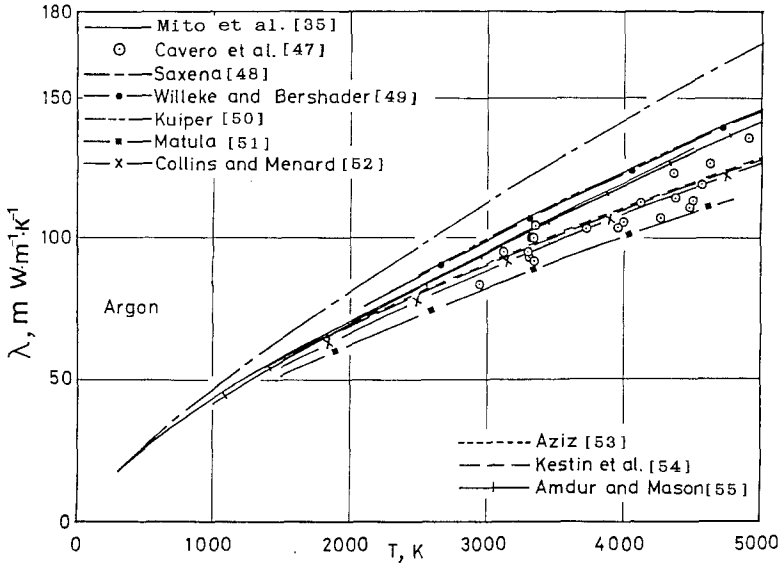


Fig. 12. Thermal conductivity of argon.

over a wide range of temperatures was determined. Our results showed good agreement with recent theoretical values at temperatures below 2000 K but not at higher temperatures.

7. CONCLUDING REMARKS

At the technology frontier, demands for thermophysical property data of high-temperature fluids are very strong. In the past, applications of simple methods which had been developed originally for a moderate temperature range produced many unreliable data at high temperatures. This has led users of thermophysical property data into confusion. Many data bases incorporated as many data as they could collect without critical evaluation or rational selection. We needed to establish reliable data bases with the aid of new experimental determinations and critical evaluations. Advanced measurement methods are needed. Since new sensors and electronic devices are invented or developed every year, regular reevaluation of methods and of reference data is desirable.

In addition to the development of new measurement techniques, several problems should be studied: (1) effect of radiation on the measurement of transport properties, (2) effect of convection on thermal conductivity (thermal diffusivity), (3) levitation technique, etc. (4) Undoubtedly, we need new techniques for measuring properties of fluids at temperatures above 2000 K.

ACKNOWLEDGMENT

The author thanks Mr. N. Nakazawa for his assistance in the preparation of the manuscript.

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