V. S. Shifrina and N. N. Samosatskii, Preparation and Use of Polyethylene [in Russian], GNTI, Leningrad (1961).

3. B. S. Sazhin and E. A. Chuvpilo, Standard Drier with Suspended Layer of Material [in Russian], TSINTIKhIMNEFTEMASh, Moscow (1975).

HIGH-TEMPERATURE CONDUCTION OF HELIUM-XENON MIXTURES

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An experimental method is described and is used to obtain new experimental data on the heat conduction of the mixtures 0.5He-0.5Xe and 0.9He-0.1Xe at high temperatures and near-atmospheric pressure.

## Introduction

Most of the problems encountered in high-temperature engineering are associated with the heat transfer in a hot gas or from a gas to a wall, and require a knowledge of thermophysical characteristics, in particular, the transfer properties of heat carriers. The heat conduction is a very important property of a material but the determination of heat conduction at high temperatures is beset by considerable difficulties.

The rigorous molecular-kinetic theory of monatomic gases gives satisfactory theoretical results for the heat conduction of mixtures of monatomic gases at moderate temperatues, and the model of molecular interactions that is used has been experimentally verified at these temperatures. At high temperatures (on the order of  $10^{3}$ °K), however, experimental verification of the theoretical calculations is lacking or incomplete.

Heat-conduction measurements at temperatures up to approximately 1500-2000°K are usually made by the fairly accurate steady-state heated-wire method and those at 6000-8000°K are made on the basis of the energy balance of a hot or quenching electric arc, measuring its characteristic and the radial temperature distribution in the arc column. The region between 1500 and 6000°K has had little methodical investigation; almost the only method that can be used is to investigate the nonsteady heat transfer in the temperature boundary layer of the gas heated by the reflected shock wave at the end of the shock tube. The advantage of the method is the purely thermal homogeneous preheating of the gas. The measurements are made by the contact method (the temperature at the end surface) or optically (the temperature profile in the temperature boundary layer of gas at the end of the tube).

### 2. Formulation of Problem, Method

With regard to both the procedure and the specific techniques of the experiment, determining the heat conduction by the shock-tube method is complicated, since it involves the investigation of a high-temperature medium in a thin (on the order of  $10^{-4}$  m) temperature boundary layer with a large temperature gradient (of the order of  $10^{6}-10^{7}$  K/m) in an extremely short time interval ( $10^{-7}-10^{-4}$  sec).

In this interval, a number of physical and chemical processes that may affect the experimental results are occurring in the gas. It is customary, in dealing with these measurements, to make a number of a priori assumptions, which are found to be satisfactory for many gases over a sufficiently wide range of temperature and pressure; the heat-conduction data in the literature are based on these assumptions. They are as follows: that there is local thermodynamic equilibrium in the gas; that the heat transfer is one-dimensional; that the thickness of the temperature boundary layer is small in comparison with the length of the hot-gas column; that the pressure in the gas at the end of the tube is zero; that the radiation of the gas does not depend on the coordinate and is negligibly small; and that the accommodation of the gas energy at the wall is complete.

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Fig. 1. Temperature boundary layer at the end of the shock tube (RSW denotes the reflected shock wave).

However, in a number of theoretically and practically important cases several of these assumptions have not been verified. Therefore, in collaboration with the thermophysical laboratory of the A. V. Lykov Institute of Heat and Mass Transfer of the Academy of Sciences of the Belorussian SSR, some methodically important properties were investigated, in particular, the influence of the diffusional thermoeffect on heat-conduction measurements in gas mixtures. It is well known that thermodiffusion is insignificant in the steady-state heatedwire method. However, it has not been known how the diffusional thermoeffect influences the heat transfer in the presence of steep temperature gradients and strongly nonsteady conditions. This question was considered in [1], where it was shown that the diffusional thermoeffect should be insignificant in these conditions. In addition, it was shown that the theoretical results obtained using the Chapman-Cowling theory are equivalent to, and may be compared with, experimental data obtained by steady-state methods and by the nonsteady shocktube method.

The present paper is devoted to the experimental verification of these theoretical results.

### 3. Experimental Results

So as to prevent the screening of the diffusional thermoeffect by other effects, it is desirable to choose a mixture for which this effect is particularly pronounced, the experimental conditions are clearly defined, and theoretical monitoring of the experiment is possible. The most suitable is a mixture of Lorentz type or quasi-Lorents type (a small quantity of heavy particles in a light gas); for monatomic gases, a mixture of helium and xenon. To eliminate the effect of incomplete thermal accommodation, the effect of which may be quite significant, measurements were made at various pressures.

For comparison, experiments were made with mixtures of two concentrations: 0.9He-0.1Xe and 0.5He-0.5Xe, for which the diffusional thermoeffect is maximum.

The experimental procedure was described in [3]. After the shock wave is reflected from the end of the shock tube, the temperature at the end surface changes; measurements of this temperature difference form the basis for the contact method of determining the heat conduction (Fig. 1).

From the basic equations of continuity and energy conservation (which are sufficient, given the above assumptions, to describe the phenomena in the temperature boundary layer)

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x} \left( \rho \omega \right) = 0, \tag{1}$$

$$\rho c_p \left( \frac{\partial T}{\partial t} + w \; \frac{\partial T}{\partial x} \right) = \frac{\partial}{\partial x} \left( \lambda \; \frac{\partial T}{\partial x} \right), \tag{2}$$

by simple transformations it is possible to derive the boundary-layer equation

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Fig. 2. Experimental apparatus: HP) high-pressure chamber of shock tube; LP) low-pressure chamber of shock tube; D) diaphragm; M1, 2, 3) manometer; O) oscillograph; MB) measurement bridge; RT) resistance thermometer; TC1, 2, 3) time counters; PA1, 2, 3) pulse amplifiers; P) piezoamplifier; ST1, 2, 3) signal thermometers.

TABLE 1. Experimental Values of  $\lambda$  for He-Xe Mixtures at Atmospheric Pressure and Various Temperatures

T, *K	$\lambda \cdot W/m \cdot K$	
	0,5 He-0,5 Xe	0,9 He-0,1 Xe
1500 2000 3000 4000 5000 6000	0,130 0,159 0,208 0,253 0,297 0,344	0,358 0,435 0,575 0,687 0,798 0,915

$$\frac{d^2\theta}{dy^2} + 2\frac{c_p^2}{c_{pg}}\frac{y}{\beta}\frac{d\theta}{dy} = 0,$$
(3)

where

$$\beta(\theta) = \lambda \rho c_p / (\lambda \rho c_p)_g; \tag{4}$$

$$\theta = \frac{1}{\lambda_{g} \rho_{g}} \int_{r_{g}}^{T} \lambda \rho dT$$
(5)

and the coordinate

$$y = \frac{\int_{0}^{x} \rho dx}{2\rho_{\rm g} \sqrt{a_{\rm g} t}} .$$
 (6)

Approximate solution of Eq. (3) for the gas at the wall gives

$$\left(\frac{d\theta}{dy}\right)_{g} = \frac{2}{\sqrt{\pi}} \int_{T_{g}}^{T_{s}} \sqrt{\beta} \, dT.$$
(7)

The change in temperature of the wall surface is determined by the relation

$$\left(\frac{d\theta}{dy}\right)_{\rm W} = \frac{2}{\sqrt{\pi}} \sqrt{\frac{(\lambda\rho c)_{\rm W}}{(\lambda\rho c_{\rm g})_{\rm g}}} (T_{\rm g} - T_{\rm o}). \tag{8}$$

Hence, Eqs. (7) and (8) lead to a formula for the heat conduction:

 $\lambda = \frac{(\lambda \rho c)_{W}}{\rho c_{p}} \left[ \left( \frac{\partial f(T_{5}; p_{5})}{\partial T_{5}} \right)_{p} \right]^{2}, \qquad (9)$ 



Fig. 3. Experimental results for 0.5He-0.5Xe (a) and 0.9He-0.1Xe (b) treated by the method of least squares. T, °K.

which is the basis for the treatment of the experimental data. For contact measurements by a film resistance thermometer, the thermometer signal  $\Delta E$  is recorded by an oscillograph with a photoattachment and, for a potential E at the measurement bridge, is introduced in Eq. (9) as follows:

$$\lambda = \frac{k_{\rm W}}{\rho c_p} \left[ \frac{d \left( \frac{\Delta E \sqrt{p}}{E V \overline{p_5}} \right)}{dT_5} \right]^2. \tag{10}$$

After differentiation of the temperature dependence in Eq. (10) by the method of least squares, the heat conduction is expressed directly as a function of temperature. The constant  $k_W$  is obtained from data for  $\lambda$  measured by another (independent) method or, as in the present case, results calculated theoretically in the reference temperature interval 1000-1500°K.

The measurements were made in a shock tube of constant circular cross section (diameter 0.05 m, length 8 m) with an aluminum diaphragm. The experimental apparatus is shown in Fig. 2. The working gas was hydrogen or an  $H_2$  - Ar mixture with a maximum pressure on the order of 1 MPa. The test mixtures were prepared from pure helium (for nuclear engineering) and xenon [of All-Union State Standard (GOST) purity] by isothermal mixing. In addition to the measurement of the temperature at the end surface by means of a precision thin-film resistance thermometer, in the bridge circuit the shock-wave velocity was measured (with an accuracy of around 0.5%) by a thin-film instrument of another type. The pressure behind the reflected shock wave was measured by a Kistler quartz piezorecorder (with accuracy up to 5%). The readings were recorded using an oscillograph and an electronic counter. The parameters of the gas mixture behind the incident wave ( $p_2$ ,  $T_2$ ) and the reflected shock wave ( $p_5$ ,  $T_5$ ) were calculated from the measurements of the initial pressure of the mixture and the velocity of the shock wave front by the method of [8]; the product of  $\rho$  and  $c_p$  at temperature  $T_5$  was calculated from the equation of state of the mixture and the reflected data of [9].

### 4. Discussion of Results

For the mixture 0.5He -0.5Xe, 96 measurements were made in the temperature range  $\sim 1700-7400$ °K and the pressure range 0.5-0.43 MPa. For the mixture 0.9He -0.1Xe 110 measurements were made in the temperature range  $\sim 1300-6260$ °C and the pressure range  $\sim 0.02-0.27$  MPa.

The curves obtained for the two mixtures after treating all the points by the method of least squares are shown in Fig. 3. The results for  $\lambda$  are given in Table 1 and Fig. 4. The accuracy of the experimental results for  $\lambda$  is  $\sim 10\%$ .

Curves 1 in Fig. 4 give experimental data for the two mixtures. Curves 2 and 3 give theoretical results for two different potential functions of the molecular interaction: Curve 3 corresponds to the Lennard-Jones potential (6-12) with parameters  $\sigma_{\text{He}} = 2.576$  Å,  $\varepsilon_{\text{He}}/k = 10.22^{\circ}$ K and  $\sigma_{\text{Xe}} = 4.082$  Å,  $\varepsilon_{\text{Xe}}/k = 206.9^{\circ}$ K [4]; curve 2 is calculated using the Buckingham



Fig. 4. Heat conduction of He-Xe mixtures: 1) present experiment; 2) theoretical data for the potential (exp-6) [7]; 3) theoretical data for the Lennard-Jones potential (6-12).  $\lambda$ , W/m•°K.

potential (exp-6) with the best combination of parameters for helium [5] and xenon [6] recommended in [7]. The experimental temperature dependence of the heat conduction in the range up to 2000°K (curve 2) was used to determine the reference region for the treatment of the measurements, since the potential (exp-6) is a good representation for the heat conduction of the pure components of the mixture.

It is evident from Fig. 4 that curve 3 lies considerably below the other results (including those not shown here). This confirms the assumption that the description of the behavior of the mixtures using the Lennard-Jones potential (6-12) is probably not sufficiently reliable. The experimental results (curve 1) for the two mixtures lie approximately 3% below the theoretical results (curve 2) calculated for the potential (exp-6). The discrepancy is very small and lies within the limits of experimental error even without taking the diffusional thermoeffect into account.

The diffusional thermoeffect is found to be insignificant. According to these results, the thermodiffusional component  $\lambda_D^T$  of the heat conduction for the mixture 0.5He-0.5Xe reaches around 3% in the worst case and for 0.9He-0.1Xe around 1% of the value of  $\lambda$  over the whole temperature range investigated.

The good agreement of the experimental and theoretical results indicates that the Buckingham potential (exp-6) with appropriate parameters is probably the best model for the heat conduction of the He-Xe mixtures at high temperatures. This agreement and the fact that the discrepancy between curves 1 and 2 is approximately the same for the two mixtures confirms the theoretical conclusion that the diffusional thermoeffect does not significantly influence heat-conduction measurements for binary mixtures of inert gases by the nonsteady shock-tube method.

This result is methodically important both as regards the possibility of using shock tubes for investigations in this region and with reference to the quality of the new experimental results obtained in the present work.

#### NOTATION

 $\alpha$ , thermal diffusivity; w, gas velocity in shock tube;  $k_w$ , instrumental constant;  $\lambda$ , heat conduction;  $\rho$ , density; t, time; T, thermodynamic temperature; x, coordinate;  $c_p$ , isobaric molar specific heat; k, Boltzmann constant. Indices: g, gas (at temperature of end surface); w, wall (end) of shock tube (at temperature of surface); p, at constant pressure; 0, at time t  $\leq 0$ ; 5, gas state after reflection of shock wave (outside temperature boundary layer); 2, gas state behind incident shock wave.

#### LITERATURE CITED

 A. G. Shashkov, T. N. Abramenko, O. A. Kolenchits, and É. V. Ivashkevich, "Transfer properties of material," in: Heat and Mass Transfer [in Russian], Vol. 7, ITMO Akad. Nauk BSSR, Minsk (1972).

- A. G. Shashkov, J. Maštovský, T. N. Abramenko, E. I. Marchenkov, O. A. Kolenchits, and V. I. Aleinikova, Acta Tech. ČSAV, <u>20</u>, 564 (1975).
- 3. J. Maštovský and F. Slepička, Z. Wärme- und Stoffübertragung, 3, 237 (1970).
- 4. E. A. Mason and H. von Ubisch, Fluids, <u>3</u>, 355 (1960).
- 5. K. T. Shin and W. E. Ibele, Heat Transfer (TASME-C), 90, 413 (1968).
- 6. E. A. Mason, Chem. Phys., 23, 49 (1955).
- 7. T. N. Abramenko, O. A. Kolenchits, T. P. Anokhina, V. I. Aleinikova, and E. V. Ivashkevich, Report of the Agreed Plan for Two-Level Cooperation between the A. V. Lykov Institute of Heat and Mass Transfer of the Academy of Sciences of the Belorussian SSR and the Institute of Thermomechanics, Czechoslovakian Academy of Sciences [in Russian], Minsk (1972).
- 8. V. Kmoniček, Acta Tech. ČSAV, 17, No. 5, 542 (1972).
- 9. V. P. Glushko, Thermodynamic Properties of Individual Materials. Handbook [in Russian], Vol. 2, Izd. Akad. Nauk SSSR, Moscow (1962).

# THERMAL CONDUCTIVITY OF BINARY AND TERNARY DISORDERED SOLID SOLUTIONS OF A TITANIUM-ZIRCONIUM-HAFNIUM SYSTEM

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Measurements of thermophysical properties of ternary alloys of a Ti-Zr-Hf system are presented. The possibility of generalizing such results and predicting the thermal conductivity of ternary continuous disordered solid solution is shown.

In [1] it was demonstrated that the method of structure modeling and calculation of effective (phenomenological) generalized conductivity coefficients in multicomponent mechanical mixtures could be generalized to calculation of thermal conductivity of nonmechanical mixtures, including binary alloys with continuous and limited component solubility in the solid state.

It is thus of interest to verify the possibility of using the method of structure modeling and calculation of effective properties for prediction of thermal conductivity of ternary continuous disordered solid solutions, and to verify the possibility of using this method for checking and generalizing measurement results.

We will consider a ternary system, the components of which form continuous disordered solid replacement solutions within the Gibbs concentration triangle (Fig. 1). We divide the total area of concentration triangle ABC into four triangles designated I-IV. In triangle I components B and C are the impurities, replacing atoms of the major component A at its lattice points. In Fig. 1 at a certain distance from vortex A we introduce a cutting plane passing through points M and N, perpendicular to the plane ABC and parallel to the base BC. At any point K on the straight line MN the total number of impurity atoms B and C in the lattice of the ternary solution remains constant, and the position of the point K characterizes the concentration ratio of components B and C. At the extreme point M the concentration of component C becomes equal to zero (atomic concentration  $x_{\rm C} = 0$ ) and the ternary system reduces to a binary solid solution AB with thermal conductivity  $\lambda_{\rm AB}^{\rm M}$ . At the point N where the atomic concentration  $x_{\rm C}$ .

We assume that the C impurity atoms introduce into the crystalline lattice of the major component A perturbations which are larger (scattering thermal energy carriers more intensely) than those produced by the B impurity atoms, as a result of which the thermal conductivity  $\lambda_{AC}^{N}$  of the binary solid solution at point N is less than the thermal conductivity  $\lambda_{AB}^{M}$  at point M. Then motion of the point K along the line MN is equivalent to gradual replacement of component B impurity atoms by component C, introducing larger perturbations into the crystalline

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