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LINEAR EFFECTS OF THE ENERGY TRANSFER IN GASES

T. N. Abramenko, V. I. Aleinikova, M. V. Sagarda, and N. E. Kuz'mina

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The authors discuss the linear effects of energy transfer in a gas that can attain a steady state and the linear similarity theory based on geometric transformations preserving the distance between points.

Transport phenomena in gases appear when the random motion of molecules becomes ordered due to temperature and velocity gradients etc. imposed on the investigated gas system. The transport phenomena can be described in terms of the thermodynamics of irreversible processes, which relates fluxes I_i with thermodynamic forces x_i. It is generally assumed that near thermodynamic equilibrium, the linear relations for the fluxes and thermodynamic forces are, in a first approximation,

$$I_i = \sum_{j=1}^{2} L_{ij} X_j . \tag{1}$$

Here the proper phenomenological coefficients L_{ii}, L_{jj} are always positive while the mutual coefficients L_{ij}, L_{ji} can have any sign [1]: $L_{ij} > 0$, $L_{jj} > 0$, $L_{ij} = L_{ji}$.

There is a large group of systems that satisfy this assumption. In such systems the linear effects of transfer are manifested, the phenomenological coefficients L_{ii}, L_{ij} are linear functions of the parameters of state and the systems themselves are stationary (the mass flow is equal to zero).

The geometric structure of a gas is a set of elements (molecules) with a given type of relations between them that are determined by the rate of energy transfer. In a steady-state gas, the rate of energy transfer is infinite:

$$I_q = -\lambda \nabla T , \quad \lambda = (L_{22} - U^{*2} L_{11})/T^2 .$$

This relation is known as the Fourier law, which is of a purely heuristic nature and is used to determine the thermal conductivity of a steady-state gas.

The space of states of a system is a metric space ("metric" means the presence of length) where any parameter of the system can play the role of distances between two points (two states of the system) [2]. Note that any thermodynamic process is a path into the space of states.

The linear effects of transfer are determined in the Euclidean space of states.

The linear similarity theory of transfer processes is a theory based on geometric transformations in which the distance between two points is specified and which is valid in the case of linear metric spaces.

Two physical processes are said to be similar if they obey the same laws and all physical quantities characterizing one process can be transformed into quantities characterizing another process by simple multiplication of the former by constant coefficients, which are called similarity coefficients [3].

According to [4], a "dimensionless" description of the temperature dependence of the transfer coefficients from the viewpoint of the phenomenological theory of thermodynamic similarity is based on formulas of the type:

Institute of Applied Physics of the Academy of Sciences of Belarus, Academic Scientific Complex "A. V. Luikov Heat and Mass Transfer Institute of the Academy of Sciences of Belarus," Minsk, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 68, No. 5, pp. 793-798, September-October, 1995. Original article submitted February 18, 1994.

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TABLE 1. T and λ Values at the Critical Point

Gas	T_{cr}, K	λ_{cr}, W/(m·K)
Ne	44.5	0.0033
Ar	151.2	0.0030
Kr	209.4	0.0021
Xe	289.8	0.0017

$$\frac{Y}{Y^*} = f(\tau), \tag{2}$$

where Y is the transfer coefficient; Y^* is a parameter with Y dimensionality composed either of critical data or of molecular parameters.

We now determine the extent to which relation (2) is valid over a wide temperature range. For this, in [5] the thermal conductivities of argon, neon, krypton, and xenon were generalized in the temperature range of 90–7000 K by the relation

$$\lambda^* = \frac{\lambda}{\lambda_{cr}} = f(T/T_{cr}), \tag{3}$$

where λ_{cr}, T_{cr} are the variables at the critical point (Table 1).

In performing the generalization, results [6-15] for Ar, [8-11, 13-15] for Ne, [8, 9, 11-14] for Kr, [9-11, 13, 16-18] for Xe were used.

Processing of the indicated thermal conductivities by the least-squares method with the aid of the polynomial

$$\ln \lambda^* = \sum_{i=1}^{3} c_i (\ln T^*)^{i-1} \tag{4}$$

allowed the experimental data to be described in the following temperature ranges: 160–7000 K, $\ln T^* = -0.5-4.0$ for Xe; 129–7000 K, $\ln T^* = -0.5-4.0$ for Kr; 90–7000 K, $\ln T^* = -0.5-4.0$ for Ar; 120–2500 K, $\ln T^* = 1.0-4.0$ for Ne with an error of 0.5–3.5% by a single generalized curve with the following coefficients: c_i = 1.1822; 0.8739; −0.0415 at i = 1, 2, 3, respectively (with the exception of the thermal conductivity of argon at T = 90.34 K [6] and xenon at T = 194.74 K [9]: the error attains 5.5 and 6%, respectively).

As for the thermal conductivity of neon in the low (90–120 K) and high (2500–6000 K) temperature ranges, its reduced value is systematically overestimated by up to 6% with respect to the generalized dashed curve (Fig. 1a).

To clarify a behavior of the temperature-dependent thermal conductivity of neon, a method of reduction with the aid of molecular parameters was used [19]:

$$\lambda^* = \frac{\sigma^2 m^{1/2}}{\varepsilon^{1/2} k} \lambda = f(T^*), \quad T^* = \frac{Tk}{\varepsilon}. \tag{5}$$

Processing of the reduced values by the polynomial dependence

$$\ln \lambda^* = \sum_{i=1}^{4} c_i (\ln T^*)^{i-1} \tag{6}$$

allowed the experimental data to be described in the following temperature ranges: 165–2500 K, $\ln T^* = -0.3-2.4$; for Kr, 120–2500 K, $\ln T^* = -0.46-2.6$; for Ar, 90–2500 K, $\ln T^* = -0.3-3.1$; for Ne, 115–850 K,

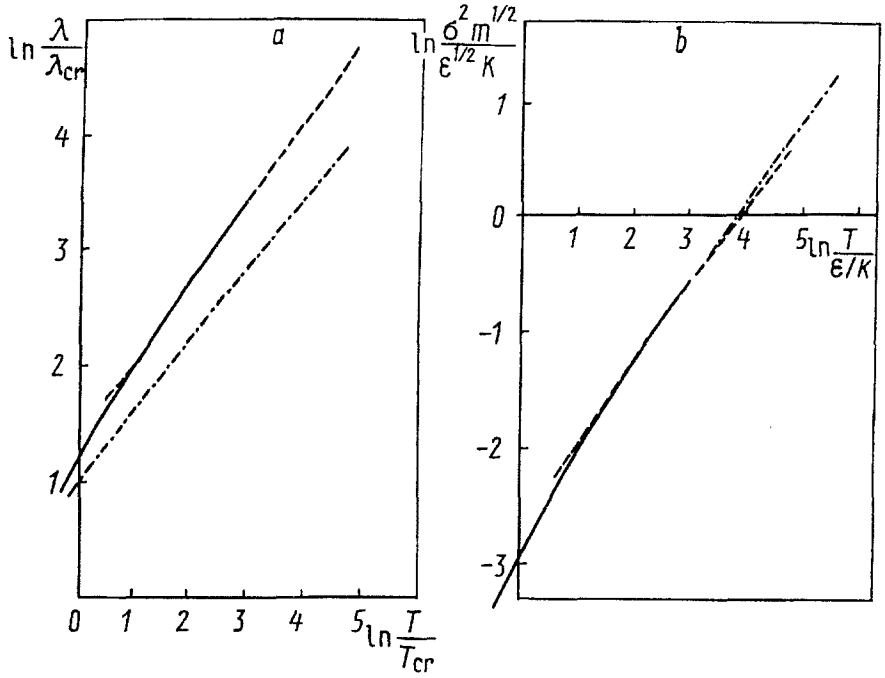

Fig. 1. Dimensionless presentation of experimental data on the thermal conductivity of gases: solid line, argon, krypton, xenon; dot-and-dash line, helium.

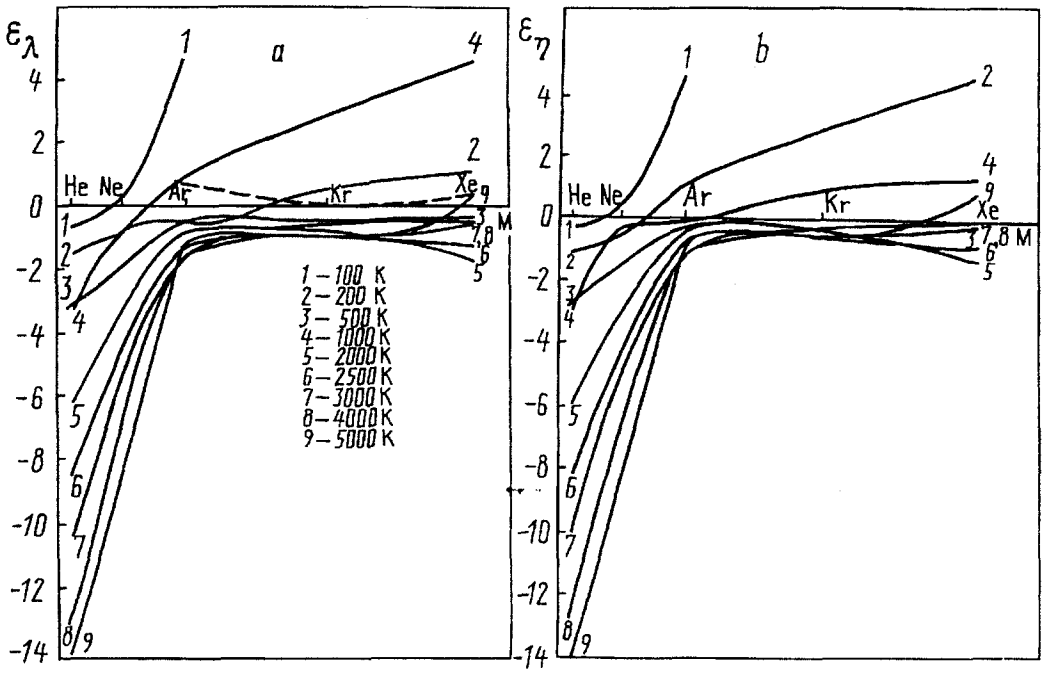

Fig. 2. Deviation of the data [26] on thermal conductivity ($\varepsilon_\lambda = (\lambda_{[26]} - \lambda_{exp})/\lambda_{exp}$, %) (a) and viscosity ($\varepsilon(M) = (\eta_{[26]} - \eta_{exp})/\eta_{exp}$, %) (b) vs molecular weight of gases.

ln T^* = 1.0–3.0 with an error of 0.5–2.0% by a single generalized curve with the following coefficients: c_i = −2.9162; 0.9435; −0.0893; 0.0095 at i = 1, 2, 3, 4, respectively.

Thus, peculiar behavior of the thermal conductivity of neon was revealed: in the temperature range 30–115 K (ln $T^* < 1.0$) the reduced values are overestimated, but in the range 850–2500 K (ln $T^* > 3.0$) they are underestimated relative to the curve characterizing the generalized dependence (6) (Fig. 1b). The deviation is ~6%, i.e., beyond the limits of the error of experimental data (the mean absolute deviation of the thermal

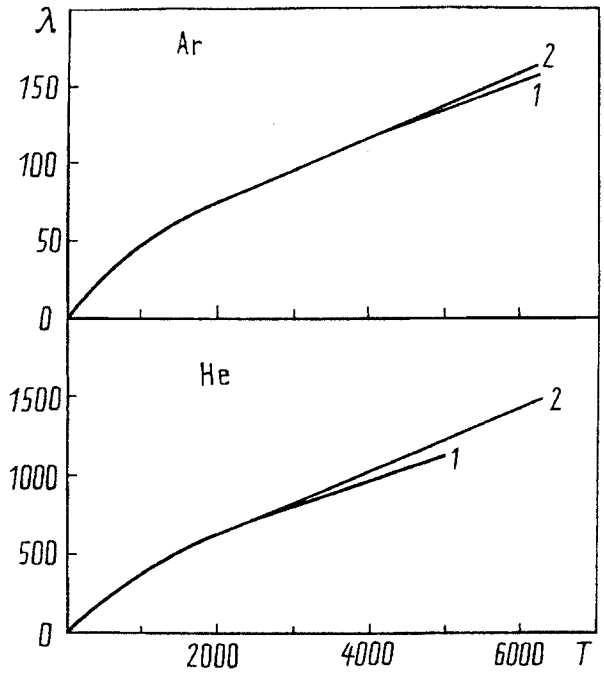

Fig. 3. Comparison of the experimental thermal conductivity values of argon and helium [27] (1) with generalized data [26] (2).

conductivities of neon, calculated by formula (4) for the temperature ranges of 90–120 K and 2500–6000 K and by formula (6) for temperatures of 850 to 2500 K from the experimental values is also 6%).

Finally, we analyze the temperature dependence of the thermal conductivities of helium, the lightest of the inert gases, by using relations (3) and (5). Consideration of the experimental data [9-11, 14, 16, 20-25] in the temperature range of 5–2500 K ($\ln T^* = -0.71 - 5.49$) revealed the following:

After reduction to the critical parameters ($T_{cr} = 5.3$ K, $\lambda_{cr} = 0.0061$ W/(m·K), the temperature dependence of thermal conductivity is described by the curve

$$\ln \lambda^* = 0.5598 + 0.6668 \ln T^* \tag{7}$$

(the maximum error is 4%), which is strongly underestimated relative to the curve of relation (4) (Fig. 2a);

After generalization with the aid of potential parameters (Eq. (5)), the relation of the thermal conductivities in the temperature range of 5–340 K is described by curve (6) (an error of 2%); at $T > 340$ K ($\ln T^* > 3.5$) the deviation from the values obtained by (6) reaches 10% (Fig. 2b).

In [26], using the hypothesis that all potentials of the intermolecular interaction of inert gases can be made congruent by the corresponding selection of scaled parameters, the authors constructed a unified intermolecular interaction potential and used it to calculate the thermal conductivity and viscosity of monoatomic gases. The quantity $\varepsilon_\lambda = (\lambda_{[26]} - \lambda_{exp})/\lambda_{exp}$ is the higher, the lighter the gas under consideration (see Fig. 2a). The dependence $\varepsilon_\eta(M) = (\eta_{[26]} - \eta_{exp})/\eta_{exp}$ (Fig. 2b) behaves in the same manner. Thus, the result obtained in [26] does not contradict our conclusions (Fig. 2): the lighter the gas, the more complicated the "dimensionless" description of the temperature-dependent thermal conductivities.

A comparison of experimental data on the thermal conductivity of helium and argon [27] with the generalized data [26] (see Fig. 3) shows overestimation of the latter. Thus, none of the considered modifications of the similarity theory allows experimental data to be described sufficiently fully.

NOTATION

L_{ii}, L_{ij}, phenomenological coefficients; x_i, thermodynamic forces; I_q, specific heat flux; U^*, transfer energy; T, temperature; T^*, reduced temperature; λ, thermal conductivity of the local-equilibrium gas; λ^*, reduced thermal

conductivity; k, Boltzmann constant; ε, σ, parameters of the intermolecular interaction potential; m, molecular weight.

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