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Gas-Phase Transport Phenomena at Low Temperatures: Thermal Diffusion in an Ar–Kr System

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A metal two-bulb apparatus for the measurement of the thermal diffusion factor, α_T, especially at temperatures below room temperature, has been designed and constructed. The results for the argon-krypton system are reported, and these cover five mixture compositions (25, 40, 50, 60, and 75% of krypton). The top bulb is maintained at 293.2 K, while the temperature of the lower bulb is varied in the range 102–250 K. The measured α_T values are estimated to be accurate within $\pm 4\%$. The positive minimum in the present α_T values is less pronounced than that reported by some other workers, and this is attributed to the operating conditions and to the apparatus geometry.

KEY WORDS: argon; dimerization; kinetic theory; krypton; low temperatures; mixtures; thermal diffusion.

1. INTRODUCTION

The theory of gas-phase transport phenomena in spherically symmetric gases at moderate temperatures and pressures of multicomponent systems is well understood and is adequately summarized in the classical works of Chapman and Cowling [1] and Hirschfelder et al. [2]. The extensions of this kinetic theory to describe thermal conductivity and thermal diffusion phenomena in polyatomic gases and gas mixtures have not always satisfactorily survived the tests provided by direct experimental data. We have, therefore, initiated a

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detailed program for the measurement of thermal conductivity of gases and gas mixtures at high temperatures (Shashkov et al. [3]) and at low temperatures (Shashkov et al. [4]), and of thermal diffusion (Shashkov et al. [5]) under the USA–USSR collaborative research program. The last work dealt with the design, fabrication, and test of an apparatus to measure thermal diffusion factors for gas mixtures at temperatures above room temperature. In particular, the experimental data for six binary gas pairs were reported as a function of temperature and mixture composition. Here, we report the details of an experimental facility appropriate for the accurate determination of thermal diffusion separation of gas mixtures at temperatures below room temperature. As a check of the experimental arrangement, the data obtained for the binary mixtures of argon–krypton are reported. The five mixtures investigated contain 25, 40, 50, 60, and 75% of krypton. In each case, the top bulb of the two-bulb apparatus is maintained at 297.2 K, while the temperature of the bottom bulb is varied in the maximum range of 102–250 K.

There has been considerable interest in the thermal diffusion data for the argon–krypton system as a positive minimum, as reported by Grew and Mundy [6], in whose work the thermal diffusion factor, α_T, is plotted versus temperature, T. Such a dependence of $\alpha_T(T)$ was observed in this work for the first time. This dependence, is further confirmed at least qualitatively by Humphreys and Mason [7], who have also questioned the accuracy of α_T measurements of Grew and Mundy [6] at temperatures lying roughly between 90 K and room temperature. The most elaborate work on this system is that of Grew and Wakeham [8], who have investigated four mixture compositions containing 9.85, 29.62, 49.98, and 79.97% of krypton in the maximum temperature range of 96.0–273.1 K. They have inferred that the temperature at which the minimum occurs increases with the increase in the proportion of krypton in the mixture. They also point out the feeble dependence of α_T on the composition of the mixture at a fixed temperature. However, the uncertainties of their experimental data did not allow for establishing any systematic trend, except at the lowest temperature. These workers find the earlier two efforts as generally supporting their data and conclusions [6, 7]. Some of the less elaborate measurements on this system are those of Grew [9], Grew et al. [10], and Santamaria et al. [11]. Recently, Taylor [12] has reported α_T data for this system as obtained on a 20-tube trennschaukel for an equimolar mixture in the approximate temperature range of 200–800 K and as a function of composition at 250 K. These measurements, therefore, do not cover the combination of those temperatures and compositions at which a positive minimum in α_T is observed by the workers referred to above.

The thermal diffusion separations reported here refer to wide enough temperature and composition ranges and will be able to provide some insight into the explanation of this α_T behavior, which has been somewhat puzzling. This is primarily because the observed α_T temperature dependence is very uncommon and has not been predicted by kinetic theory on the basis of intermolecular potential functions, which have been successful in correlating the various equilibrium and nonequilibrium properties of this system. We also examine the evidence available in the literature to explain this unique temperature dependence of α_T on the basis of the formation of dimers at low temperatures, adsorption of krypton on the walls of the apparatus, and the choice of the intermolecular potential functions.

2. EXPERIMENTAL APPARATUS AND PROCEDURE

The detailed schematic of the experimental arrangement, consisting of the gas supply tanks, gas mixing cylinders, two-bulb apparatus, cryostat, and the constant temperature bath with its liquid circulation system, vacuum pump, and gauges, etc. is shown in Fig. 1. The important details of the two-bulb metal apparatus are shown in Fig. 2, while those of the top bulb itself are shown in Fig. 3. The upper part of the apparatus is a brass metal block (*1*), into which two symmetric cavities, V_1 and V_2, each having a volume 8.8 cm^3, have been drilled. These cavities are connected to the vacuum line and the gas handling system through high vacuum values; see Fig. 1. The cavity V_1 constitutes the top bulb of the two-bulb apparatus. The bottom bulb, V_b, *3* in Fig. 2, is also made of brass and has a volume of 281.6 cm^3 and $V_b/V_1 = 35$. To the bottom bulb, V_b, is welded an outer metal jacket, *4* in

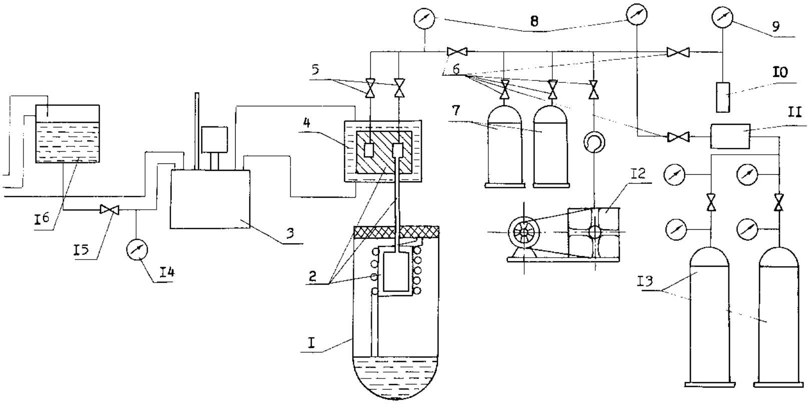

Fig. 1. A schematic diagram of the experimental arrangement. *1*, cryostat; *2*, two-bulb apparatus; *3*, thermostat; *4*, water bath; *5*, *6*, *15*, valves; *7*, gas mixing cylinders; *8*, pressure gauges; *9*, ionization gauge; *10*, vacuum tube; *11*, drying agent; *12*, rotary pump; *13*, gas cylinders; *14*, manometer; *16*, feed tank.

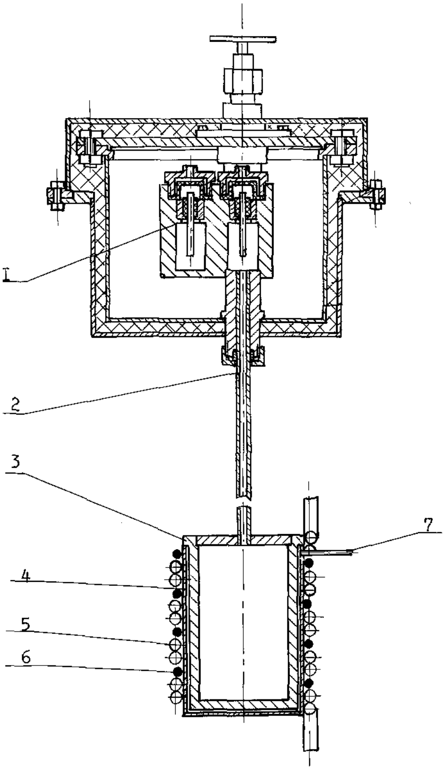

Fig. 2. A schematic diagram of the two-bulb apparatus. *1*, top bulb; *2*, connecting tube; *3*, bottom bulb; *4*, upper jacket; *5*, heat exchanger; *6*, heater; *7*, side tube.

Fig. 2, such that an air gap of 1 mm is left between the two. Surrounding the jacket is the heat exchanger, *5* in Fig. 2, consisting of a 4.5-mm i.d. copper tube, and a ceramic insulated electrical heater, *6* in Fig. 2. The air gap between the bulb (*3*) and the outer jacket (*4*) serves as a gas thermometer and is connected through the side tube (*7*) to a temperature controller. The entire bottom bulb is immersed in a liquid nitrogen cryostat, and its temperature is controlled by regulating the boiling rate of liquid nitrogen. Three copper-constantan thermocouples are embedded along its height. During experiments, the temperatures indicated by the central and the two end thermocouples did not differ by more than 0.6 K around 150 K and by about 5 K near 105 K.

The top and bottom bulbs are connected together by a 20 cm long, 0.4 i.d. stainless steel tube, *2* in Fig. 2. The volume of the connecting tube is 2.51

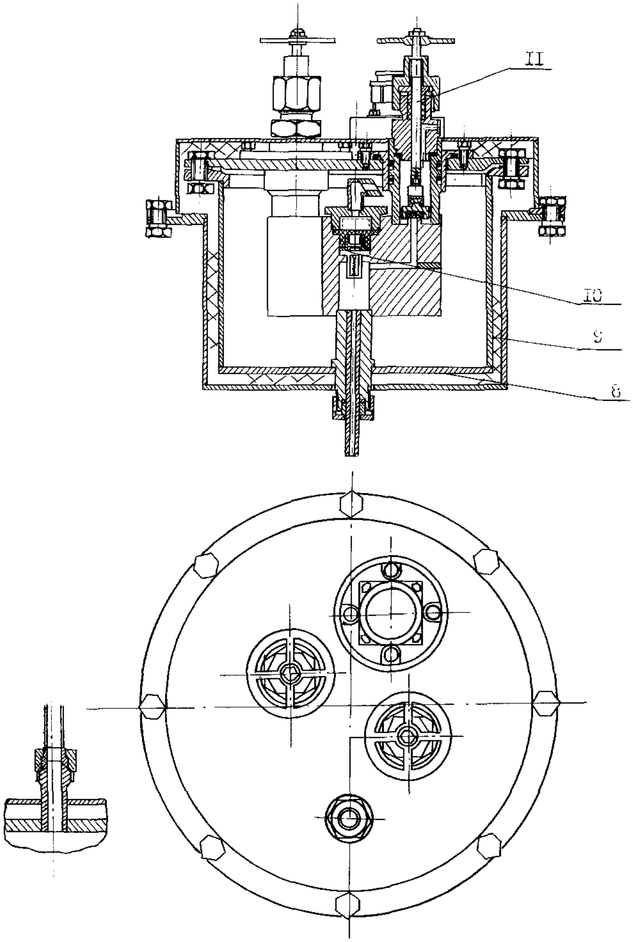

Fig. 3. A schematic diagram of the top bulb of the two-bulb apparatus. *8*, water bath; *9*, asbestos insulation; *10*, sensitive element; *11*, vacuum valve.

cm^3. Foam plastic is wrapped around this tube to insulate it thermally from the surroundings. The top block is mounted inside a stainless steel water bath, whose temperature is maintained constant at 293.2 ± 0.01 K. The inner surface of the cavities V_1 and V_2 and the bottom bulb are thoroughly polished to reduce gaseous adsorption. This is important, for krypton adsorption on the cold bulb walls is employed to explain the positive minimum observed in the values of α_T for the argon–krypton system.

The katherometer method of gas analysis based on the dependence of thermal conductivity on gas mixture composition is well established. The method is simple and allows in situ analysis, and therefore is superbly appropriate for the present work. Plantinum wire resistances serve as sensitive elements, and these are characterized by their high stability, long life, and high sensitivity. These resistances are platinum spirals of diameter 0.3 ± 0.1 mm and are mounted inside the cavities V_1 and V_2 of the upper block. At 293.2 K, their resistances are 20.766 and 20.772 ohms. The use of two elements successfully eliminates such effects as heat loss via the supporting leads, radiative and convective heat transfer, etc. The value of the current through the coils is chosen such that the temperature difference between the sensitive elements and the surrounding medium is about 20 K. These sensitive elements are fed from two 12 V current stabilized power supplies. The volumes V_1 and V_2 are filled with the same initial mixture while the elements remain heated.

At the beginning of an experimental run, the two bulbs are brought to the same initial temperature. The upper block is maintained at a temperature that is only 0.3 K above the room temperature. The entire apparatus is evacuated to a pressure of about 4×10^{-5} Torr, flushed with the test gas mixture, and is evacuated again. The two cavities (V_1 and V_2) and the bottom bulb (V_b) are filled with the gas mixture at an initial pressure of about 380 Torr. Next, the cryostat is filled with liquid nitrogen and the bottom bulb is cooled to the desired temperature. The voltage difference between the sensitive elements is periodically measured as it characterizes the thermal separation. The steady state is assumed to have reached when the change in voltage difference during an hour is within the potentiometer sensitivity, i.e., 0.001%. Further details may be found in Zhdanov and Zolotukhina [13].

3. RESULTS

The purity of argon and krypton employed in the present measurements is 99.987 and 99.99%, respectively. If the temperatures of the hot and cold bulbs are represented by T_H and T_C, respectively, then α_T can be computed by the following relation:

$$\alpha_T = \frac{1}{X_1 X_2} \frac{dS}{d[\ln (T_H/T_C)]} \tag{1}$$

Here X_1 and X_2 are the mole fractions of the heavier and lighter components, respectively. Further, the separation, S, for our apparatus geometry may be computed as the difference of the initial and final percentage concentrations of the heavier component (krypton) in the top bulb at temperature T_H ($>T_C$). These values are listed in Table I. Two qualitative trends are apparent from Table I. First, for mixtures containing more than 40% krypton, there is a large increase in the thermal separation when the bottom bulb temperature is

Table I. Experimental Values of Thermal Diffusion Separation, S, for the Argon–Krypton System[a]

	X_1				
T_c(K)	0.25	0.40	0.50	0.60	0.75
250	0.1970	0.2472	0.2398	0.2298	0.1741
210	0.3748	0.4628	0.4326	0.4127	0.3109
170	0.5040	0.6143	0.5758	0.5555	0.4280
150	0.5549	0.6923	0.6458	0.6183	0.4882
130	0.6130	0.7675	0.7249	0.6876	0.5277
110	0.6731	0.8422	0.7972	0.7593	0.5755
106					0.9222
105		0.8694			
104				1.2010	
103			0.8571		
102	0.6992				
100			1.1740		

[a] $T_H = 297.2$ K. Gas mixture pressure is 0.5 bar (5×10^5 dyn/cm^2).

less than 110 K. Second, for T_C between 110 and 250 K, the thermal diffusion separation decreases as the proportion of the heavier component in the mixture increases. In order to calculate α_T from Eq. (1), the experimental S values have been represented by suitable polynomials in the powers of ln (T_H/T_C), viz.,

$$S = \sum_{n=1,5} A_n \{\ln (T_H/T_C)\}^n \tag{2}$$

The constants A_n of Eq. (2), as determined by the method of least-squares, are given in Table II for all the five mixtures having different proportions of krypton. The measured 32 S values have been correlated on the basis of Eq. (2) within an average absolute deviation of 0.7%. The four data points

Table II. Constants A_n of Equation (2)

	A_n				
X_1	A_1	A_2	A_3	A_4	A_5
0.25	0.01128	+0.01111	−0.05272	+0.05743	−0.02033
0.40	0.01542	+0.00356	−0.04309	+0.05223	−0.01961
0.50	0.01489	+0.00578	−0.05755	+0.07738	−0.03241
0.60	0.01485	−0.00111	−0.03228	+0.04400	−0.01774
0.75	0.01190	−0.00919	+0.00344	−0.00037	0.00000

referring to the lowest temperatures have not been considered. The maximum and minimum deviations are 1.3 and 0.06%, respectively. Equation (2) is therefore considered accurate enough to be used in conjunction with Eq. (1) for the calculation of α_T. The estimated experimental uncertainty of α_T is always less than 4%. In Table III, these values of α_T are recorded for all the five mixtures and as a function of temperature of the cold bulb, T_C.

The accurate extensive measurements of Grew and Wakeham [8] cover the cold bulb temperature in the range 96.0 to 273.1 K and are for four different compositions of the mixture. The hot bulb temperature is maintained at 300 K, and the mole fractions of krypton in the mixture are 9.85, 29.62, 49.98, and 79.97%. Their data are compared with the present data in Fig. 4, where the observed thermal diffusion separations are plotted as a function of ln (T_H/T_C). The agreement is regarded as satisfactory. Reference may now be made to the more recent measurements of Taylor [12]. He found that for an equimolar mixture, the α_T values are best represented by the following function in the approximate temperature range 200–800 K:

$$\alpha_T = 0.4854 - (10.76/T^{1/2}) + (61.90/T) \tag{3}$$

Computed values of α_T from Eq. (3) are reported in the seventh column of Table III. It is to be noted that in so doing, we have employed Eq. (3) outside the temperature range for which it is originally developed. Consequently, any comparison has to be only approximate in nature. These values are in general agreement with our data, and therefore our present work lends confirmation to the proposed correlation of Eq. (3) as the most probable α_T values for the wide temperature range. These values exhibit a positive minimum in the α_T values at low temperatures. Our thermal diffusion separation data listed in Table I also suggest a positive minimum.

Table III. Experimental Values of α_T for the Ar–Kr System[a]

	X_1					
T_c, K	0.25	0.40	0.50	0.60	0.75	Eq. (3)
250	0.0635	0.0581	0.0534	0.0523	0.0487	0.0525
210	0.0439	0.0408	0.0355	0.0360	0.0362	0.0376
170	0.0324	0.0250	0.0227	0.0229	0.0249	0.0242
150	0.0205	0.0217	0.0223	0.0206	0.0200	0.0194
130	0.0200	0.0216	0.0192	0.0202	0.0158	0.0179
110	0.0189	0.0181	0.0151	0.0142	0.0128	0.0222
105		0.0144				0.0248
102	0.0124					0.0268

[a] $T_H = 297.2$ K.

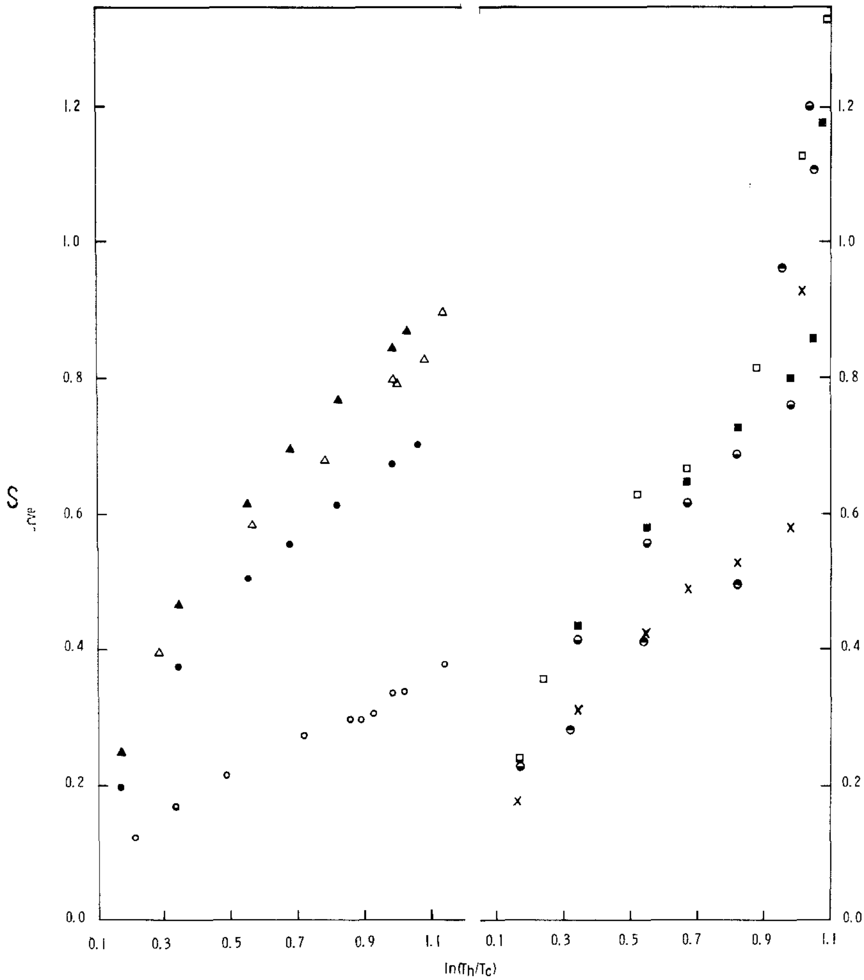

Fig. 4. Observed separation as a function of ln (T_H/T_C) for different mixtures of krypton and argon. Present data: ● 25% Kr, ▲ 40% Kr, ■ 50% Kr, ⊖ 60% Kr, and × 75% Kr. Grew and Wakeham [8]: ○ 9.85% Kr, △ 29.62% Kr, □ 49.98% Kr, and ● 79.97% Kr.

4. DISCUSSION

The representation of α_T for this system as a function of temperature and composition has attracted a lot of attention. The kinetic theory in conjunction with simple intermolecular potentials has not accomplished this task successfully, as a positive minimum in the α_T data at low temperatures has been observed by many workers, such as Grew and Wakeham [8]. The failure of simple potentials such as Lennard-Jones (12–6), modified Buckingham exp-six, Kihara core, and Morse potential models is evident from the works of Grew and Mundy [6] and Humphreys and Mason [7]. Nain and Aziz [14] have examined all the available gas-phase macroscopic data on second virial, viscosity, and diffusion coefficients and have proposed three hybrid intermolecular potentials. These are Lee–Henderson–Barker (LHB), Morse-6 (MO6), and Gough–Matthews–Smith–Maitland (GMSM) potentials. These relatively complicated potentials have also not succeeded in reproducing quantitatively the α_T data over the entire temperature range. Taylor [12] concludes from his analysis of the α_T data for all the ten binary systems of five noble gases that the Dymond-Alder [15] numerical potential with the parameters given by Lim and Robinson [16] is adequate. He also employs the third approximation expression for thermal diffusion factor. The interpretation of low temperature α_T data must take into account the formation of dimers, so that an apparent binary system transforms into a ternary system when only one of the two components (mostly heavier) undergoes incipient dimerization. The composition of this ternary system will depend upon the temperature and pressure. The necessary details of such a calculation have been developed in a series of papers by Van der Valk [17], Oost and DeVries [18], and Wakeham [19]. The theoretical calculations of Wakeham [19], taking into account the presence of dimers, do show a positive minimum in α_T.

In our data, reported in Tables I and III, α_T is found to decrease systematically as the temperature is decreased for all the five mixtures. Further, at a fixed temperature, as the proportion of krypton in the mixture is increased, α_T is found to decrease. The decrease is much smaller for mixtures containing a larger amount of krypton, and also at low temperatures. All these qualitative trends are well known; they can be explained on the basis of available data, and also by the simple Chapman–Enskog kinetic theory (Grew and Ibbs [20]).

The present thermal diffusion separation values are somewhat lower than the data reported by Grew and Wakeham [8]; see Fig. 4. This suggests that on the basis of present data, a more shallow positive minimum in α_T at a much lower temperature of the bottom bulb would be obtained than that claimed by Grew and Wakeham [8]. The reason for this is that for the operating conditions (temperature and pressure) and the geometry (volumes of the two bulbs and their ratio) of the apparatus employed in our work, the concentration of dimers is negligible (Wakeham [19]). As is well known and explicitly detailed by Wakeham [19], the positive minimum in α_T is due to the formation of dimers. When the temperature of the cold bulb was further lowered below 100 K, and the pressure of krypton was approximately equal to the saturation vapor pressure of krypton, a sudden increase in thermal separation was observed (Zhdanov [21]). This enhancement in separation implies a sudden increase in α_T and gives rise to a positive minimum. We thus find our present data in complete accord with the available data in the literature. These data also suggest that formation of dimers plays an important role in α_T measurements at low temperatures, in conformity with the suggestion of Mathur and Watson [22].

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REFERENCES

1. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Cambridge, U.K., 1970).
2. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1964).
3. A. G. Shashkov, E. I. Marchenkov, V. I. Aleinikova, R. Afshar, R. K. Joshi, and S. C. Saxena, *Proc. 15th Int. Conf. Thermal Conductivity,* Ottawa, Ontario, Canada, August 24–26, 1977, V. V. Mirkovich, ed. (Plenum, New York, 1978), pp. 223–234.
4. A. G. Shashkov, T. N. Abramenko, N. A. Nesterov, R. K. Joshi, R. Afsher, and S. C. Saxena, *Chem. Phys.* **29:**373 (1978).
5. A. G. Shashkov, A. F. Zolotukhina, T. N. Abramenko, B. P. Mathur, and S. C. Saxena, *J. Phys. B: Atom. Molec. Phys.* **12:**3619 (1979).
6. K. E. Grew and J. N. Mundy, *Phys. Fluids* **4:**1325 (1961).
7. A. E. Humphreys and E. A. Mason, *Phys. Fluids* **13:**65 (1970).
8. K. E. Grew and W. A. Wakeham, *J. Phys. B: Atom. Mol. Phys.* **4:**1548 (1971).
9. K. E. Grew, *Proc. Roy. Soc. (London)* **A189:**402 (1947).
10. K. E. Grew, E. A. Johnson, and W. E. J. Neal, *Proc. Roy. Soc. (London)* **A224:**513 (1954].
11. C. M. Santamaria, J. M. Saviron, and J. C. Yarza, *Physica* **83A:**615 (1976).
12. W. L. Taylor, private communication.
13. V. L. Zhdanov and A. F. Zolotukhina, *Study of Heat and Mass Transfer Processes in Substances with Different Aggregate States* (Izd. ITMO AN BSSR, Minsk, 1977).
14. V. P. S. Nain and R. A. Aziz, *Mol. Phys.* **33:**203 (1977).
15. J. H. Dymond and B. J. Alder, *J. Chem. Phys.* **51:**309 (1969).
16. H. M. Lim and R. L. Robinson, Jr., *J. Chem. Phys.* **54:**52(1971).
17. F. Van der Valk, *Physica* **29:**417 (1963).
18. W. A. Oost and A. E. De Vries, *Physica* **41:**440 (1969).
19. W. A. Wakeham, *J. Phys. B: Atom. Mol. Phys.* **4:**1564 (1971).
20. K. E. Grew and T. L. Ibbs, *Thermal Diffusion in Gases* (Cambridge University Press, London, 1952).
21. V. L. Zhdanov, *Vesti An BSSR, Ser. Fig. Energy Nauk,* **4** (1978).
22. B. P. Mathur and W. W. Watson, *J. Chem. Phys.* **51:**2210, 5623 (1969).