# ISOCHORIC THERMAL CONDUCTIVITY OF ARGON, KRYPTON, XENON, AND NITROGEN AS A FUNCTION OF THE TRIPLE POINTS UP TO 300-330°K AT PRESSURES OF UP TO 3000 atm

V. P. Slyusar', V. M. Tret'yakov,
and N. S. Rudenko

UDC 536.22+536.23

We investigate the isochoric thermal conductivity of Ar, Kr, Xe, and $N_2$, and, in the critical region, we estimate the critical indicators of thermal conductivity. The experimental results are compared with conclusions drawn from the kinetic theory.

A great deal of attention is being given nowadays to the study of the kinetic properties of liquefied inert gases, nitrogen, methane, and oxygen. This interest is due to the fact that these substances have a spherical or near-sperical symmetry in their molecules and little or no quantum effect; this facilitates the theoretical investigation of their properties. Moreover, the rapid development of low-temperature techniques requires an exact knowledge of the kinetic coefficients of cryogenic liquids and their dense gases.

In the present study we measured the isochoric thermal conductivity of liquefied inert gases and of nitrogen in the liquid and dense gaseous phases, from temperatures close to the triple points to 300-330°K, and from densities close to triple-point densities to gas densities at a pressure of 1 atm. On the basis of these measurements, we investigated the behavior of the thermal conductivity as a function of the temperature or the density, and we also compared the experimental results with the conclusions drawn from the kinetic theory.

Isochoric Thermal Conductivity. Prior to the investigation conducted in this study, the thermal conductivities of Ar, Kr, Xe, and $N_2$ had been measured near the saturation curve or in the region of room temperature and higher temperatures. There were no measurements at high pressures up to 3000 atm in the intermediate temperature range. No investigations had been conducted along the saturation curve, and there were only a few studies for Ar [1,2] in the critical region. The literature contained no information on the isochoric thermal conductivity of these substances, and all available data had been obtained by various methods in narrow ranges of temperature and pressure variation along isotherms or isobars (Fig. 1). For this reason, we conducted investigations over a wide range of temperatures and pressures. Our measurements were made by the hot-wire relative method at constant volume (density). The measurement error outside the critical region was estimated at 3.5-4%, and in the critical region at 10-30% [3-5]. The range of variation of PVT values for the measurements of the thermal conductivity of Ar, Kr, Xe, and $N_2$, as well as some parameters of these substances used below, are shown in Table 1.

In all the substances investigated, we discovered general laws governing the behavior of the isochoric thermal conductivity as a function of temperature. As an example, we show in Fig. 2 the results of the measurements for argon. The thermal conductivity of argon along the saturation curve, as can be seen from Fig. 2, decreases for a liquid and increases for a vapor. The behavior of the thermal conductivity of liquids on the saturation curve far from the critical temperature for all of the substances investigated can be satisfactorily described by the empirical equation

$$\lambda = \lambda_{tr} + B(T - T_{tr}), \qquad (1)$$

where T is the instantaneous temperature; B is a coefficient determined from the measurement data. The thermal conductivity along an isochore outside the critical region increases monotonically, as in a gas at a pressure of 1 atm, but much more slowly than with increasing density:

---

Kharkov Physicotechnical Institute, Academy of Sciences of the Ukrainian SSR. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 38, No. 4, pp. 628-633, April, 1980. Original article submitted April 6, 1979.

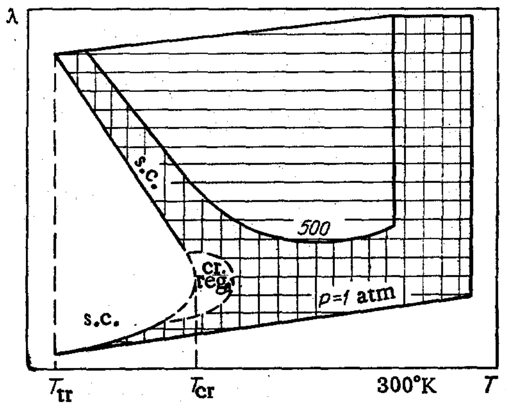

Fig. 1

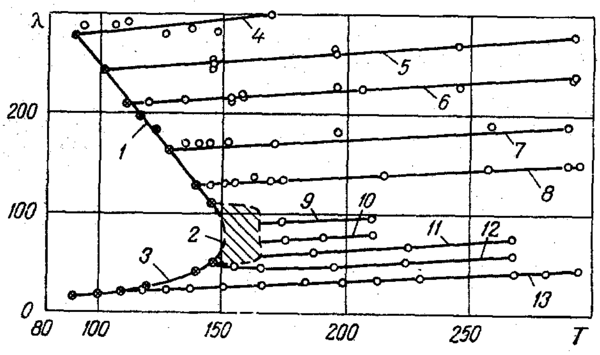

Fig. 2

Fig. 1. Regions of investigation of thermal conductivity: shading perpendicular to the temperature axis indicates the measurements of earlier authors; shading parallel to the temperature axis indicates our measurements; s.c. indicates the saturation curve; cr. reg. indicates the critical region; $T_{tr}$, $T_{cr}$ are the temperatures of the triple and critical points.

Fig. 2. Isochoric thermal conductivity of argon as a function of temperature: 1) liquid at the saturation curve; 2) critical region; 3) vapor at the saturation curve; 4) $\rho$ = 1.372 g/cm³; 5) 1.300; 6) 1.224; 7) 1.080; 8) 0.932; 9) 0.699; 10) 0.554; 11) 0.432; 12) $\rho$ = 0.276 g/cm³; 13) P = 1 atm.

$$\frac{1}{\lambda}\left(\frac{\partial\lambda}{\partial T}\right)_{\rho=\mathrm{const}} < \frac{1}{\lambda}\left(\frac{\partial\lambda}{\partial\rho}\right)_{T=\mathrm{const}}. \tag{2}$$

The values of the derivatives $(\partial\lambda/\partial T)_{\rho=\mathrm{const}}$ were calculated on the isochores for temperature T and density $\rho$; those of the derivatives $(\partial\lambda/\partial\rho)_{T=\mathrm{const}}$ were calculated on the isotherms at the same temperature and density. For small values of the densities the values of the derivatives are identical, but as the density increases, the difference increases, and at densities close to the triple-point density the derivatives differ by one order of magnitude or more. This evidently indicates that the main contribution to the thermal conductivity is made by the change in density and not by the change in temperature. Formula (2) was considered for all the substances investigated in the form given above. To do this, we used the parameters of the Lennard-Jones potential that are shown in Table 1.

From the experiment, we found the excess values of the isothermal thermal conductivity $\Delta\lambda$ as a function of the density according to the equation

TABLE 1. Variation of PVT Values for the Measurements, and Some Molecular Constants of the Substances Investigated

| Parameters | Substance | | | |
|---|---|---|---|---|
| | $N_2$ | Ar | Kr | Xe |
| Temp. range of meas., °K | 64,2—300 | 90—300 | 120—300 | 180—330 |
| Variation in density, g/cm³ | 0,067—0,864 | 0,078—1,372 | 0,344—2,424 | 0,200—2,846 |
| No. of isochores (isopycnics) | 18 | 23 | 13 | 13 |
| Pressure variation from 1 atm | 3000 | 2630 | 2730 | 1380 |
| Temp., °K: | | | | |
| triple point, $T_{tr}$ | 63,15 | 83,81 | 115,78 | 161,36 |
| critical point, $T_{cr}$ | 126,21[6] | 150,72 [7] | 209,4 [8] | 289,74 [9] |
| Density, g/cm³: | | | | |
| at triple point, $\rho_{tr}$ | 0,869 | 1,410 | 2,443 | 2,977 |
| at critical point, $\rho_{cr}$ | 0,311 | 0,536 | 0,911 | 1,100 |
| Parameters of Lennard-Jones potential: | | | | |
| $\varepsilon/k$, °K, | 95 [10] | 119,5 [11] | 166,67 [11] | 230,0 [12] |
| $\sigma\cdot10^8$ cm | 3,70 [10] | 3,409 [11] | 3,681 [11] | 3,920 [12] |
| Reduced De Broglie wavelength, $\Lambda^*$ | 0,225 [12] | 0,187 [12] | 0,102 [12] | 0,064 [12] |
| Thermal conductivity at triple point, $\lambda_{tr}\cdot10^6$, cal/cm·sec·deg | 384 | 309 | 224 | 183 |

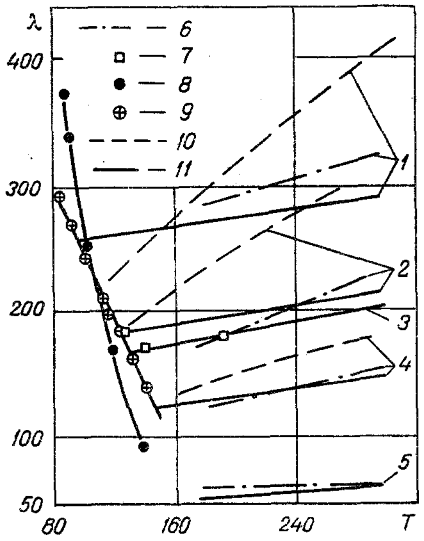

Fig. 3. Comparison of calculated and measured thermal conductivities of argon on the saturation curve and along the isochores: 1) $\rho = 1.31$; 2) 1.16; 3) 1.12; 4) 0.354; 5) 0.078 g/cm$^3$; 6) Enskog [13,14]; 7) Ikenberry and Rice [15]; 8) Prigogine et al. [16,18]; 9) Eyring et al. [17]; 10) Lagar'kov and Sergeev [19]; 11) experiment. $\lambda \cdot 10^6$, cal/cm·sec·deg; T, °K.

$$\Delta\lambda = \lambda_{(\rho,T)} - \lambda_{(\rho_0,T)}, \tag{3}$$

where $\lambda_{(\rho,T)}$ is the thermal conductivity on the isochore at temperature T and density $\rho$; $\lambda_{(\rho_0,T)}$ is the thermal conductivity of the gas at P = 1 atm and the same temperature. No stratification of the isotherms of the excess thermal conductivity for all the investigated substances is observed within the limits of experimental error [3-5]. The excess isothermal thermal conductivity is satisfactorily described by a series in the density, proposed by N. B. Vargaftik:

$$\Delta\lambda = \sum_{a=1}^{N} B_a \rho^a,$$

where the $B_a$ are coefficients determined from the experimental data for each substance; N is an integer; $a$ is a parameter which, for the error in our experiments, it is sufficient to vary from 1 to 4. The absence of any stratification of excess thermal conductivity and the formula (2) support the belief that the contribution to the total transfer made by the kinetic energy of the particles is much less than the contribution made by the potential part. This conclusion agrees with the results of theoretical investigations [13-16].

The isochoric thermal conductivities of Ar, Kr, Xe, and $N_2$ measured in our study were recomputed with the aid of the PVT values, and their values were compared with the results obtained by other authors along the isotherms as a function of density or pressure. The comparison shows that in the overlapping intervals our measurements agree with the data obtained by the parallel-plate and coaxial-cylinder methods.

The thermal conductivity along the isochores, as indicated above, has the same type of temperature dependence, and therefore it was of interest to consider the results obtained from the viewpoint of the law of corresponding states. The reduction was made by the de Boer scheme [12], where the coefficients of the thermal conductivity, temperature, and density were expressed in terms of the parameters $\varepsilon$ and $\sigma$ of the Lennard-Jones potential, whose values are shown in Table 1. The variation of the given thermal conductivities as functions of the reduced temperature for the saturation curve and along five reduced isochores for Ar, Kr, and Xe can be described, within the limits of measurement error, by the same curves [5]. The reduced thermal conductivity of nitrogen is not described by these curves, probably because the molecules of $N_2$ have a symmetry different from those of the molecules of inert

TABLE 2. Critical Temperatures and Critical Exponents for the Thermal Conductivity of Ar, Kr, Xe, and $N_2$

| Substance | $T_{cr}$, °K | $a$ | $\lambda_0 \cdot 10^6$, cal/cm·sec·deg |
|---|---|---|---|
| Ar | 126,21 [6] | 0,76±0,10 | 14,5±2,0 |
| Kr | 150,72 [7] | 0,68∓0,05 | 16,7∓2,5 |
| Xe | 209,4 [8] | 0,62∓0,06 | 14,5∓2,2 |
| $N_2$ | 289,74 [9] | 0,69∓0,07 | 15,8±2,6 |

gases. Using the law of corresponding states, we calculated the thermal conductivities of neon and radon along the isochores and up to the saturation curve [5]. From the analysis carried out in [5] it follows that the thermal conductivities of Ar, Kr, and Xe in the measured temperature and density ranges can be described by universal functions within the framework of the law of corresponding states.

Comparison of Experiment with Theory. The characteristics of the comparison made on the saturation curve and along the isochores for Ar, Kr, Xe, and $N_2$ can be seen from the example of argon (Fig. 3). We observed satisfactory agreement (within 6%) between the measurement data and the data calculated on the saturation curve for the theory of Eyring et al. [17]. From a comparison of the experiment with the results obtained by calculation according to the theories of Enskog [13,14], Ikenberry and Rice [15], Prigogine and Rice [15], and Prigogine et al. [16,18], we found that the best agreement was observed in the case of the Enskog theory. The reason for this is that the calculations of the distribution function used the equation of state and experimental PVT data. From the theories of [13-16, 18] it follows that the main contribution to the thermal conductivity is made by the term resulting from the potential energy of the interacting particles. Upon comparison with calculations made by the method of molecular dynamics [19], satisfactory agreement with the experimental data is observed for low densities, whereas for high densities the agreement with the experimental data is only qualitative.

From a comparison of the measurement data with the calculated data it follows that the thermal conductivity of liquids and dense gases can be qualitatively described by means of existing ideas concerning the thermal motion of particles [13].

Thermal Conductivity in the Critical Region. In our measurements of the thermal conductivity of $N_2$, Ar, Kr, and Xe in the neighborhood of the critical temperature for near-critical densities [3] we observed that the conductivity increases sharply. This is apparently due to the interaction of anomalously growing fluctuations [20], since according to the estimates we made in [3], the gravitational effect, the temperature gradient, and the impurities cannot affect these measurements. From experimental data in the $T > T_{cr}$ region, the thermal conductivity in the critical region can be described by the power law $\lambda = \lambda_0 t^{-a}$, where $t = (T - T_{cr})/T_{cr}$; $\lambda_0$ was found from the experimental data; $a$ is the critical exponent. From the experimental data, by graphical processing, we determined the critical exponents for all the investigated substances, which are shown in Table 2.

The errors in determining the critical exponents are due to the large measurement errors near the critical temperature and to the inaccuracy in the determination of the critical temperature itself, whose value was taken from [6-9]. These errors have a considerable effect on the determination of the critical exponents, especially in the region of low values of t [20]. The values of the critical exponent for Ar and Xe were compared in [3] with the values found by other authors in experiments on the scattering of light [21,22]. For Ar we observed satisfactory agreement, while for Xe the value of the critical exponent was 0.2 higher than the value obtained in [22]. Since we find in the literature a considerable divergence in the determination of the critical exponents and since there is no agreement [23,24] concerning the essence of the observed "anomalies" in thermal conductivity in the critical region, it becomes necessary to conduct further investigations in order to clarify the nature of the phenomena observed.

## LITERATURE CITED

1. B. J. Bailey and K. Kellner, "The thermal conductivity of liquid and gaseous argon," Physica, 39, No. 3, 444-462 (1968).

2. B. J. Bailey and K. Kellner, "The thermal conductivity of argon near the critical point," Brit. J. Appl. Phys., 18, 1645-1647 (1967).
3. V. P. Slyusar', V. M. Tret'yakov, and N. S. Rudenko, "Experimental investigation of the isochoric thermal conductivity of liquid and gaseous nitrogen in the 64.2-300°K range. Thermal conductivity of nitrogen in the critical region," Fiz. Nizk. Temp., 1, No. 9 (1975).
4. V. P. Slyusar', V. M. Tret'yakov, and N. S. Rudenko, "Thermal conductivity of argon at constant density and pressures up to 2600 atm," Ukr. Fiz. Zh., 22, No. 7 (1977).
5. V. P. Slyusar', V. M. Tret'yakov, and N. S. Rudenko, "Thermal conductivity of krypton and xenon at constant density and pressures up to 2700 atm. The law of corresponding states," Fiz. Nizk. Temp., 4, No. 6 (1978).
6. V. N. Zozulya and Yu. P. Blagoi, "Viscosity of nitrogen near the liquid—vapor critical point," Zh. Eksp. Tekh. Fiz. 66, 212-224 (1974).
7. C. A. Crommelin, "Isotherms of monatomic gases and of their binary mixtures. IV. Remarks on the preparation of argon. V. Vapour pressures above —140°C, critical temperature and critical pressure of argon," Comm. Leiden, No. 115, 1-16 (1910).
8. J. J. Meichuizen and C. A. Crommelin, "Vapour pressures of liquid krypton," Physica, 4, 1-4 (1937).
9. H. W. Habgood and W. G. Schneider, "PVT measurements in the critical region of xenon," Can. J. Chem. 32, 98-111 (1954).
10. E. Wilheim and R. Baltino, "Estimation of Lennard-Jones (6—12) pair potential parameters from gas solubility data," J. Chem. Phys., 55, 4012-4017 (1971).
11. R. Tufeu, B. Le Neindre, and P. Bury, "Etude expérimentale de la conductivite thermique du krypton á haute pression," C. R. Acad. Sc. Paris, 273B, 61-64 (1971).
12. J. De Boer, "Quantum theory of condensed permanent gases. I. The law of corresponding states," Physica, 14, 139-148 (1948).
13. H. N. Temperley, J. Rowlinson, and G. Rushbrooke (editors), Physics of Simple Liquids, Elsevier (1968).
14. E. McLaughlin, "The thermal conductivity of liquids and dense gases," Chem. Rev., 64, 389-426 (1964).
15. L. D. Ikenberry and S. A. Rice, "On the kinetic theory of dense fluids. XIV. Experimental and theoretical studies of thermal conductivity in liquid Ar, Kr, Xe, and $CH_4$," J. Chem. Phys., 39, No. 6, 1561-1571 (1963).
16. J. A. Palyvos, H. T. Davis, J. Misguich, and O. Nicolis, "Application of the Prigogine—Nicolis—Misguich theory of transport," J. Chem. Phys., 49, No. 1, 4088-4095 (1968).
17. S. H. Lin, H. J. Eyring, and W. J. Davis, "Thermal conductivity of liquids," J. Phys. Chem., 68, No. 10, 3017-3020 (1964).
18. G. Prigogine, G. Nicolis, and J. Misguich, "Local equilibrium approach to transport processes in dense media," J. Chem. Phys., 43, 4516-4521 (1965).
19. A. N. Lagar'kov and V. M. Sergeev, "Investigation of the kinetic coefficients of liquids by the method of molecular dynamics," Teplofiz. Vys. Temp., 11, No. 6 (1973).
20. M. A. Anisimov, "Investigation of critical phenomena in liquids," Usp. Fiz. Nauk, 114, No. 2 (1974).
21. H. D. Bale, B. C. Dobbs, J. S. Lin, and P. W. Schmidt, "X-ray scattering studies of critical opalescence in argon at constant density," Phys. Rev. Lett., 25, 1556-1559 (1970).
22. D. L. Henry, H. S. Swinney, and H. Z. Cammins, "Rayleigh line width in xenon at the critical point," Phys. Rev. Lett., 25, 1170-1173 (1970).
23. H. E. Stanley, Introduction to Phase Transitions and Critical Phenomena, Oxford Univ. Press (1971).
24. Kh. I. Amirkhanov and A. P. Adamov, "Thermal conductivity of carbon dioxide along a boundary curve and in the region of critical state," Teploenergetika, No. 7 (1963).