

THERMAL DIFFUSIVITY OF INERT GASES IN THE
VICINITY OF THE CRITICAL POINT

F. M. Gumerov, A. N. Sabirzyanov,
R. N. Maksudov, and A. G. Usmanov

UDC 536.2.023+526.23

Results are presented from an interferometric study of thermal diffusivity of argon over a wide range about the critical point using an equation based on the theory of interacting modes. The agreement of experimental and calculated thermal diffusivity values for argon provided the authors with a basis for calculating the thermal diffusivity of krypton in the vicinity of the critical point.

The goal of the present study is to describe the results of an interferometric investigation of the thermal diffusivity of argon in the vicinity of the critical point [1] on the basis of an empirical cross-over function, the form of which was determined beforehand using the theory of interacting modes [2]. Subsequent refinement and extension [3, 4] have produced the following expression for describing the singular portion of the thermal conductivity coefficient in a wide range about the critical point [5]:

$$\Delta\lambda(\rho, T) = R \frac{K_B T}{6\pi\eta\xi} \rho (c_p - c_v) F(\tau, \omega), \quad (1)$$

$$F(\tau, \omega) = \left(\frac{\rho}{\rho_{cr}}\right)^n \exp \left\{ - \left[A \left(\frac{T - T_{cr}}{T_{cr}}\right)^2 + B \left(\frac{\rho - \rho_{cr}}{\rho_{cr}}\right)^4 \right] \right\}, \quad (2)$$

where R is a universal constant (R = 1.03 in the interacting mode theory [6], R = 1.038 in the renormalization group method [7, 8], whilst the most probable experimental values are R = 1.00-1.06 [7]); n is an exponent taking on the value of 0 or 1/2 depending on the form of the equation of state used in the calculations; A, B are constants defined by the condition of best description of the experimental results.

We will note briefly that the measurements were performed with a two-beam diffraction interferometer, based on an IAB-451 Toppler device. The measurement circuit realized the model of two semi-infinite bodies with a constant thermal flux source on their contact boundary, and the nonsteady state thermal conductivity problem was solved. The fundamentals of this measurement method were presented in [9]. The authors of [11] attempted to modify the method of measuring the thermal diffusivity coefficient in order to allow simultaneous measurements of the thermal conductivity and diffusivity coefficients. For this purpose a second semi-infinite body, made of quartz, was used as a reference material. A platinum resistance thermometer was placed within a quartz plate in a plane parallel to the plane of the heater, at a specific distance from the heat source, in order to determine the character of the thermal flux distribution between the material under study and the reference and to calculate the thermal conductivity coefficient. However this model of the measurement cell did not provide results on the thermal conductivity coefficient with sufficient accuracy.

The thermal diffusivity coefficient of argon near the critical point was measured along the isotherms T = 188.14, 173.14, 163.15, 153.16, 150.90 K. The calculated error of the experimental data for an 0.95 confidence level ranged from 1.0 to 2.5%, with the exception of a narrow region of pressures near the critical isochor, where on the isotherms T = 153.16 and 150.90 K the error rose to 6.5 and 17.0%. The confidence level of the overall error contains within itself an unavoidable residue of systemic errors, a random component,

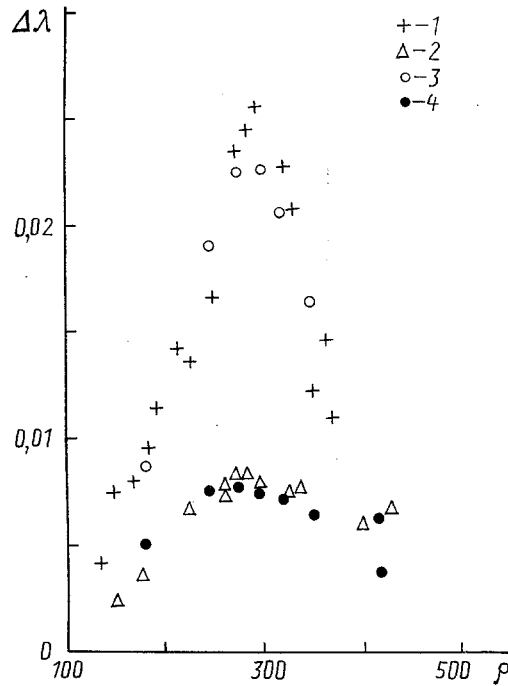


Fig. 1. Singular portion of argon thermal conductivity on isotherms: 1) 153.16 K [1]; 2) 163.15 K [1]; 3) 153.15 K [10]; 4) 163.20 K [10]. $\Delta\lambda$, W/(m·K); ρ , amaga.

and errors related to pressure and temperature references. A correction to the description of measurement results on the $T = 150.90$ K isotherm is difficult because of the high uncertainty of the data, which is the reason they were excluded from the analysis.

Direct measurements of the thermal diffusivity coefficient of argon in a wide range about the critical point had not been carried out previously. A comparison of values of the singular portion of the thermal conductivity of argon calculated from the results of the interferometric study of thermal diffusivity [1] with the equation

$$\Delta\lambda(\rho, T) = a\rho c_p - \lambda_{\text{reg}}(\rho, T), \quad (3)$$

with values obtained from the experimental study of thermal conductivity by the plane layer method [10] on isotherms with similar temperature values is shown in Fig. 1.

The thermodynamic functions of argon in calculations with Eq. (3) were defined from the equation of state proposed in [11].

The data of [11] were used to calculate the regular portion of the argon thermal conductivity:

$$\lambda_{\text{reg}}(\rho, T) = (a_1 + a_2T + a_3T^2) \sqrt{T} + (a_4 + a_5T)\rho + a_6\rho^2 + a_7\rho^3 + a_8\rho^4 + a_9\rho^5, \quad (4)$$

where ρ is the density in amaga units (1 amaga = 1.7834 kg/m³); $\lambda_{\text{reg}} \cdot 10^2$, W/(m·K).

The coefficients of Eq. (4) are as follows:

$$\begin{aligned} a_1 &= 0.3850 \cdot 10^{-8}; & a_2 &= 0.2949 \cdot 10^{-5}; & a_3 &= -0.2780 \cdot 10^{-8}; \\ a_4 &= 0.3537 \cdot 10^{-4}; & a_5 &= 0.2350 \cdot 10^{-7}; & a_6 &= 0.4465 \cdot 10^{-7}; \\ a_7 &= 0.9416 \cdot 10^{-10}; & a_8 &= -0.1217 \cdot 10^{-12}; & a_9 &= 0.2610 \cdot 10^{-15}. \end{aligned}$$

Considering that

$$c_p - c_v = \frac{T}{\rho} \left(\frac{\partial P}{\partial T} \right)_\rho^2 K_T, \quad (5)$$

we rewrite Eq. (1) in the following form:

$$\Delta\lambda_{\text{calc}}(\rho, T) = R \frac{K_B T^2}{6\pi\eta\xi} \left(\frac{\partial P}{\partial T} \right)_\rho^2 K_T F(\tau, \omega). \quad (6)$$

The final expression for describing the experimental results by Eq. (6) appears as:

$$a_{\text{calc}}(\rho, T) = \frac{\Delta\lambda_{\text{calc}}(\rho, T) + \lambda_{\text{reg}}(\rho, T)}{\rho c_P}. \quad (7)$$

We will analyze approaches to calculations with Eqs. (6) and (7).

The Ornstein-Cernike approximation [12] was used to determine the correlation length, yielding

$$\xi(\rho, T) = R_\xi \sqrt{n K_B T K_T}, \quad (8)$$

where

$$R_\xi = R_0 \sqrt{\frac{n}{K_B T}}. \quad (9)$$

Considering this fact, we transform Eq. (8) to the form

$$\xi(\rho, T) = R_0 \sqrt{n^2 K_T}, \quad (10)$$

where

$$n = \frac{N_A \rho}{\mu}, \quad (11)$$

$R_0 = 1.8 \cdot 10^{-34} \text{m}^3 \cdot \text{N}^{1/2}$ [10].

Shear viscosity values were taken from [13], in which the experimental values were presented in the form of the sum of ideal and excess viscosity components:

$$\eta(\rho, T) = \eta_0(T) + \Delta\eta(\rho, T), \quad (12)$$

where

$$\eta_0(T) = \sum_{i=10}^{10} A_i T^{(i-3)}, \quad (13)$$

$$\begin{aligned} \Delta\eta(\rho, T) = & [B_1(T - 375)^2 + C_1] \rho + \sum_{j=2}^4 C_j \rho^j + \\ & + \left(\sum_{K=2}^5 D_K \rho^K + D_9 \rho^9 \right) \frac{1}{T} + \left(\sum_{l=3}^5 E_l \rho^l + E_7 \rho^7 \right) \frac{1}{T^2}. \end{aligned} \quad (14)$$

The coefficients of Eqs. (13), (14) are as follows:

$A_1 = -88,024177686;$	$B_1 = -1,4208031984 \cdot 10^{-3};$
$A_2 = 4,3319616024;$	$C_1 = 1,2832194248 \cdot 10^2;$
$A_3 = -7,2077044082 \cdot 10^{-2};$	$C_2 = -9,6830693593 \cdot 10;$
$A_4 = 1,3654183603 \cdot 10^{-3};$	$C_3 = 3,1554546003 \cdot 10^2;$
$A_5 = -1,9171951451 \cdot 10^{-6};$	$C_4 = 7,2964230042 \cdot 10^2;$
$A_6 = 2,3694271369 \cdot 10^{-9};$	$D_2 = 1,1906669365 \cdot 10^5;$
$A_7 = -1,9077838119 \cdot 10^{-12};$	$D_3 = 1,8338168862 \cdot 10^5;$
$A_8 = 9,3733397466 \cdot 10^{-16};$	$D_4 = -9,6927431708 \cdot 10^5;$
$A_9 = -2,5414017421 \cdot 10^{-19};$	$D_5 = 5,0392874435 \cdot 10^5;$
$A_{10} = 2,9054209336 \cdot 10^{-23};$	$D_9 = -1,8043239228 \cdot 10^3;$
	$E_3 = -7,8117857565 \cdot 10^7;$
	$E_4 = 2,2526440983 \cdot 10^8;$
	$E_5 = -1,4607732241 \cdot 10^8;$
	$E_7 = 1,4709499343 \cdot 10^7.$

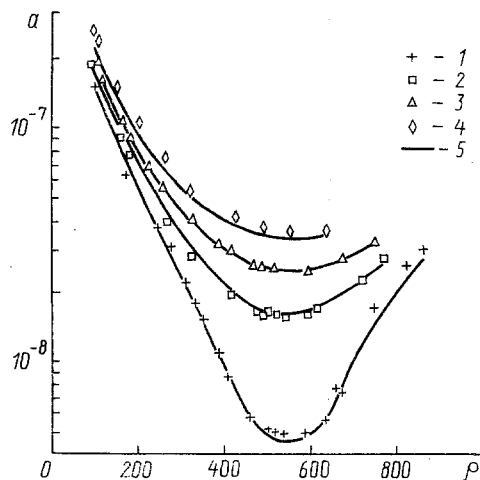


Fig. 2. Experimental and calculated thermal diffusivity values of argon vs density on isotherms: 1) 188.14 K [1]; 2) 173.14 K [1]; 3) 163.15 K [1]; 4) 153.16 K [1]; 5) calculation by Eqs. (6), (7) on above isotherms, a , m^2/sec ; ρ , kg/m^3 .

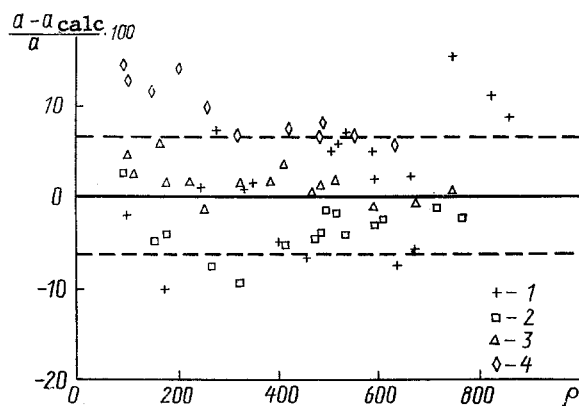


Fig. 3. Deviation of calculated values of thermal diffusivity coefficient of argon from experiment on isotherms: 1) 188.14 K; 2) 173.14 K; 3) 163.15 K; 4) 153.16 K. $a - a_{\text{calc}} \cdot 100/a$, %.

The singularity in the shear viscosity in the vicinity of the singular point was neglected. The admissibility of such an approach can be justified by the weakness of the shear viscosity anomaly, as indicated convincingly by the value of the critical index, which takes on values of the order of 0.04 [6, 14, 15, 16].

In [17] an analysis of experimental data on the thermal conductivity of carbon monoxide, argon, and methane was used to determine values of the coefficients A and B in Eq. (2). These values proved equal to 18.66 and 4.25 respectively. In that study the universality of those values was proposed. Despite the fact that subsequent studies of other materials [5] yielded different coefficients, the present study used the values presented above. Results of theoretical and experimental studies [16], indicating the existence of a wide range of universality in the vicinity of the critical point, became the source of a preference for coefficients providing a description for an entire group of substances including the object of the present study.

Critical parameters were taken from [18]: $T_{\text{cr}} = 150,725 \text{ K}$; $\rho_{\text{cr}} = 535 \text{ kg}/\text{m}^3$.

The results of the interferometric study of thermal diffusivity of argon on the isotherms $T = 188.14, 173.14, 163.15, 153.16 \text{ K}$, as well as calculations performed with Eq. (7) are shown in Fig. 2.

The mean square uncertainty in calculating thermal diffusivity comprised $\pm 6.22\%$. The character of the deviations is shown in Fig. 3. It is obvious that the main causes of divergence are the reference errors, especially with respect to pressure, between a, P, T and P, v, T data, errors in calculating the isobaric heat capacity from the equation of state, as well as inaccuracy in determining the critical temperature. Considering the fact that the uncertainty in measuring the isobaric heat capacity usually varies over the interval 3-5% and that the values determined from the equation of state, obtained from P, v, T data are no less uncertain, the agreement between the experimental and calculated thermal diffusivity values for argon can be considered satisfactory. Thus we can state that in the vicinity of the critical point the qualitative behavior of the anomalies in thermal conductivity and diffusivity can be studied with the aid of the equation of state based on Eq. (6). Based on this conclusion, a calculation of the thermal diffusivity of krypton was carried out. A review of the literature shows that other studies of the critical dynamics of krypton are practically absent.

The thermal diffusivity of krypton was studied using the equation of state proposed in [19]. This equation has a canonical form and describes the thermodynamic surface in the temperature range 120-423.15 K at pressures from 0 to 300 MPa, including the vicinity of the critical point ($T_{cr} = 209.433$ K, $\rho_{cr} = 908$ kg/m³ [19]). The correctness of the equation was tested in [19] using experimental data on isochoric heat capacity [20] and the speed of sound [21]. Comparison of calculated and experimental P, V, T data showed that the mean deviation comprised 0.058% with maximum deviation not exceeding $\pm 0.3\%$. A comparison of isobaric and isochoric heat capacities calculated with the equation of state of [19] and with results of an experimental study of the speed of sound [21] performed in [19] along the isotherms $T = 273.15, 348.15, \text{ and } 423.15$ K at pressures of 1.8-300 MPa led to the following results: the maximum deviation for isothermal compressibility and isobaric heat capacity comprised $\pm 2\%$, while that for isochoric heat capacity was $\pm 6\%$.

The results of [22] were used to obtain shear viscosity values. As in [13], in [22] viscosity was represented in the form of a sum of ideal and excess components. To calculate the ideal component [22] used the following expression:

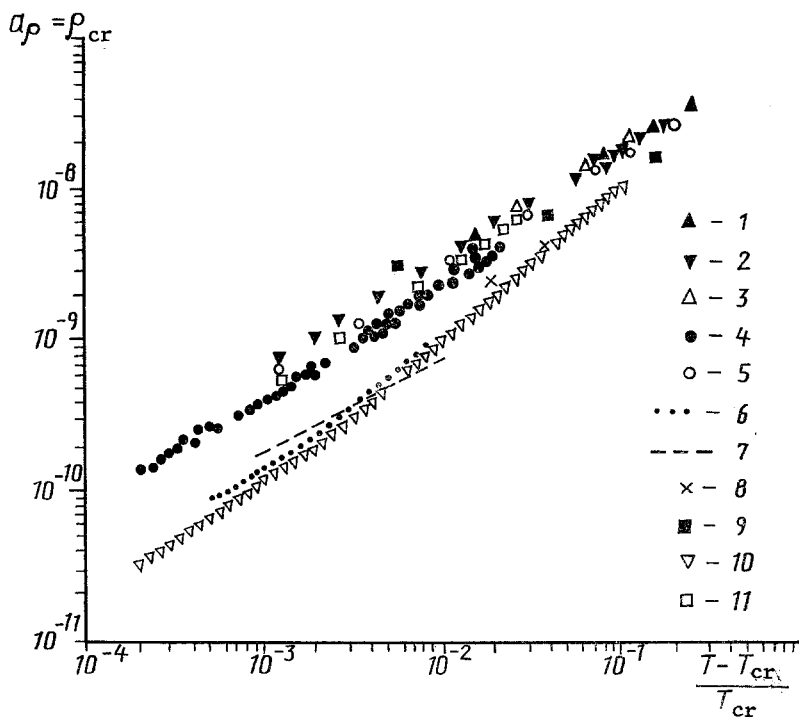


Fig. 4. Thermal diffusivity of inert gases on critical isochor: 1) Ar [1]; 2) Ar [10]; 3) Ar [24]; 4) Xe [25]; 5) Xe [26]; 6) He-3 [27]; 7) He-4 [28]; 8) He-4 [29]; 9) He-4 [30]; 10) He-3 [31]; 11) Kr (present study). a, m²/sec.

$$\eta_0(T) = A \frac{T^{2/3}}{1 + \frac{S}{T}}, \quad (15)$$

where $\eta_0(T) \cdot 10^6$, Pa·sec, $A = 0.7017$, $S = 71.93$.

The excess viscosity was calculated with the expression

$$\Delta\eta(\rho, T) = (a_1\rho + a_2\rho^2 + \dots + a_n\rho^n) \times \left(1 + K \frac{a_1\rho + a_2\rho^2 + \dots + a_n\rho^n}{T^2}\right), \quad (16)$$

where

$$a_1 = 28.032; a_2 = -111.18; a_3 = 332.46; a_4 = -420.09; \\ a_5 = 275.16; a_6 = -88.922; a_7 = 11.484; K = 19 \cdot 10^6.$$

The ideal and excess components of the regular portion of the thermal conductivity were taken from [23].

The thermal diffusivity coefficient of krypton was calculated on the isotherms $T = 209.7, 210.0, 211.0, 212.0, 213.0, 214.0, \text{ and } 215.0$ K at densities of 400-1400 kg/m³.

Because of the present lack of experimental results on thermal conductivity and diffusivity of krypton in the vicinity of the critical point, the value of a was determined by analyzing the thermal diffusivity of Ar, Xe, He-3, and He-4 on the critical isochor using data from experimental studies of thermal conductivity and diffusivity [1, 10, 24-31]. Results of this analysis are shown in Fig. 4, whence it is evident that the values obtained for gases such as Ar, Xe, Kr are quite far removed from the thermal diffusivity values of He-3 and He-4, which is probably due to the quantum nature of the latter substances. It should be added that the results of the Ar, Xe, Kr studies are consistent not only for use of various techniques (classical, Rayleigh scattering, interferometry, interacting mode theory), but also for the different substances, while the He-3 and He-4 results are somewhat contradictory.

NOTATION

P , pressure, MPa; ρ , density, kg/m³; T , temperature, K; μ , molecular weight, kg/mol; k_T , isothermal compressibility, 1/Pa; c_V , isochoric specific heat, J/(kg·K); c_P , isobaric specific heat, J/(kg·K); N_A , Avogadro's number, 1/mol; K_B , Boltzmann's constant, J/K; R_ξ , Debye damping length, m; λ , thermal conductivity, W/(m·K); $\Delta\lambda$, singular thermal conductivity, W/(m·K); λ_{reg} , regular thermal conductivity, W/(m·K); a , thermal diffusivity, m²·sec; η , shear viscosity, Pa·sec; η_0 , ideal component of shear viscosity, Pa·sec; $\Delta\eta$, excess component of shear viscosity, Pa·sec; ξ , correlation length, m.

LITERATURE CITED

1. F. M. Gumerov, D. G. Amirkhanov, and A. G. Usmanov, Heat and Mass Exchange in Chemical Technology [in Russian], Kazan' (1979), pp. 8-11.
2. G. Stanley, Phase Transitions and Critical Phenomena [Russian translation], Moscow (1973).
3. I. V. Sengers, "Transport Phenomena," in: Proc. Int. Boltzmann Centennial Seminar (1973), pp. 229-277.
4. H. I. M. Hanley, R. D. McCarty, and W. M. Haynes, Cryogenics, 15, No. 7, 413-417 (1975).
5. I. V. Sengers, Int. J. Thermophys., 6, No. 3, 203-232 (1985).
6. H. C. Burstyn, I. V. Sengers, I. K. Bhattacharjee, and R. A. Ferrel, Phys. Rev. A, 28, No. 3, 1567-1578 (1983).
7. D. Beysens, A. Bourgou, and G. Paladin, Phys. Rev. A, 30, No. 5, 2686-2703 (1984).
8. G. Paladin and L. Peliti, J. Phys. Lett., 43, No. 1, 15-20 (1982).
9. I. B. Bach and U. Griguli, Wärme und Stoffübertragung, No. 3, 44-57 (1980).
10. B. W. Tiesinga, Ph. D. Thesis, Univ. Amsterdam (1980), p. 160.
11. A. L. Gosman, R. D. McCarty, and I. G. Hust, NSRDS-NBS, 27, 1-146 (1969).
12. M. E. Fisher, J. Math. Phys., 5, No. 7, 944-962 (1964).
13. W. M. Haynes, Physics, 67, 440-470 (1973).
14. V. M. Zozula and Yu. P. Blagoi, Zh. Eksp. Teor. Fiz., 66, 212-224 (1974).

15. I. K. Bhattacharjee and R. A. Ferrel, *Phys. Rev. A*, 28, No. 4, 2363-2369 (1983).
16. M. A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* [in Russian], Moscow (1987).
17. H. I. M. Hanley, I. V. Sengers, and I. F. Fly, *Thermal Conductivity* 14 (1976), pp. 383-408.
18. J. M. H. Levelt Sengers, W. L. Greer, and I. V. Sengers, *J. Phys. Chem. Ref. Data*, 5, No. 1, 1-51 (1976).
19. J. Jusa and O. Sifner, *Acta Tech. CSAV*, No. 1, 1-32 (1976).
20. C. Gladun and F. Menzel, *Cryogenics*, 10, No. 3, 210-213 (1970).
21. N. J. Trappeniers, T. Wassenaar, and G. J. Wolkers, *Physica*, 32, 1503-1520 (1966).
22. S. A. Ulybin, V. I. Makarushkin, and S. V. Skorodumov, *Teplofiz. Vys. Temp.*, 16, No. 2, 282-288 (1978).
23. V. A. Rabinovich, A. A. Vasserman, V. I. Nedostup, and L. S. Veksler, *Thermophysical Properties of Neon, Argon, Krypton, and Xenon* [in Russian], Moscow (1976).
24. B. J. Bailey and K. Kellner, *Physica*, 39, 444-462 (1968).
25. H. L. Swinney and D. L. Henry, *Phys. Rev. A*, 8, No. 5, 2586-2617 (1973).
26. I. Van Oosten, Ph. D. Thesis, Univ. Amsterdam (1974), p. 146.
27. K. Ohbayashi and A. Ikushima, *Technical Report ISSP, Ser. A*, No. 675, 1-34 (1974).
28. K. Ohbayashi and A. Ikushima, *J. Low Temp. Phys.*, 15, No. 1-2, 33-46 (1974).
29. A. Acton and K. Kellner, *Physica*, 103B, 212-225 (1981).
30. V. B. Zhuze, G. E. Zubkov, and L. I. Cherneeva, *Inzh.-Fiz. Zh.*, 58, No. 6, 1576-1579 (1985).
31. C. E. Pittman, Ph. D. Thesis, Duke Univ. (1981), p. 238.

IMPREGNATING A HEATED FILLER WITH A NON-NEWTONIAN
FLUID

L. Ya. Kosachevskii', E. A. Kosachevskaya,
and L. S. Syui

UDC 532.546

An approximate parametric method is used to solve the planar temperature-dependent problem of continuously impregnating a heated filler with a fluid that has a power-law non-Newtonian viscosity.

Many composite materials are made by impregnating porous materials (fillers) with various fluids (binders), which than are polymerized or crystallized into a solid. The most convenient method to accelerate this process is to preheat the filler, which significantly reduces the viscosity of the binder during the impregnation. Here the fluid is held at a high temperature for only a short time, with no danger of thermal decomposition. An exact self-similar solution has been obtained [1] to the problem of using an ordinary viscous fluid for continuously impregnating a heated layer, which is drawn through a heated chamber. Because binders used in practice (resins and polymer melts) have more complex rheological properties, whose permeability differs from Darcy's law, the problem has been generalized [2, 3] to viscoplastic binders. The permeability is described by a generalized Darcy's law [4] for a linear temperature dependence of the rheological properties. An approximate parametric method was suggested to solve this (nonself-similar) problem. The method uses a cubic trinomial for the temperature profile. Here we examine an analogous problem of a power filtration law [5] for arbitrary temperature-dependence of the non-Newtonian viscosity and for more general heat-transfer boundary conditions at the surface of the filler. We also use a parametric method, but with a different representation of the temperature profile, which allows us to obtain the solution in a compact form suitable for numerical computations. The problem is solved analytically in the particular cases of small and large pressure gradients, and also for weak temperature dependence of the non-Newtonian viscosity.