THERMOPHYSICAL PROPERTIES OF ARGON[1]

A.D. Kozlov [2]

---

[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, Colorado, U.S.A.

[2] All-Russian Research Center for Standartization, Information and Sertification of Materials (VNITs SMV), 103006, Dolgorukovskaya, 21, Moscow, Russia; fax: (095) 978 68 77

ABSTRACT

Available experimental data, tables and equations for thermophysical properties of argon are systematized and critically evaluated. The new equation of state, viscosity and thermal conductivity equations were developed. The model for the Helmholtz free energy is used for developing of the unique for liquid and gaseous phases equation of state. For dynamic viscosity and thermal conductivity the unique equations are used. These equations include of viscosity or thermal conductivity of rarefied gas and excess viscosity or thermal conductivity. The excess thermal conductivity includes the regular part which is independent of the proximity to the critical point, and the separate scaling part which is substantional only in the vicinity of the critical point. For developing of the equation of state the pvt data and data on isohoric heat capacity were used at the first stage. At the second stage the data on isobaric heat capacity and velosity of sound were used in addition. Using these equations the tables on thermodynamic properties, dynamic viscosity and thermal conductivity were computed at temperatures from 85 up to 1300 K and pressures from 0.1 up to 1000 MPa for gaseous and liquid phases, including the vapor-liquid coexistance boundary. The tolerances of tabulated values for each calculated property value were calculated on the basis of the covariance matrixes for each equation. The tables were sertified by Russian Standard Reference Data Service. KEY WORDS: argon; fundamental equation; viscosity; thermal conductivity.

1. INTRODUCTION

Argon is often used as a calibration fluid for thermophysical property measurements. Although there are a large quantity of experimental data of acceptable accuracy, the Standard Reference Data tables including the data on thermophysical properties of argon existed in Russian only for its viscosity and thermal conductivity at the atmospheric pressure. In 1996 in Russian the new tables of Standard Reference Data [1] on thermophysical properties of argon are accepted. These tables are based on the new fundamental equation of state of argon and new viscosity and thermal conductivity equations. The tables include data on density, enthalpy, entropy, isobaric and isohoric specific heat, velosity of sound, dynamic viscosity and thermal conductivity at temperatures from 85 up to 1300 K and pressures from 0.1 up to 1000 MPa for gaseous and liquid phases, including the vapor-liquid coexistance curve. The compilation of these equations and tables is described below.

2. DATABASE

The experimental data on thermodynamic properties and viscosity and thermal conductivity of argon in the single-phase region and at saturation line are published in Ref. [2]-[49]. The main studies including data used for development of fundamental equation are summarised in Table 1. The last columne in this table shows the mean square deviation between the experimental and data obtained on the basis above equations.

3. THE FUNDAMENTAL EQUATION OF STATE

The fundamental equation which is created as dependence of the Helmholtz energy on the temperature and density was selected for description of thermodynamic surface of argon in the wide region of parameters including gaseous and liquid phases and satura-tion line liquid-vapor:

$$f = \sum_{j=1}^{32} b_j \exp(-\gamma_j \omega^{q_j}) \omega^{r_j} / \tau^{t_j} \qquad (1),$$

where $f = F_r/(RT)$, F_r - the nonideal part of the Helmholtz function; $\omega = \rho/\rho_c$, ω - reduced density; $\tau = T/T_c$, τ - reduced temperature; (ρ_c) and (T_c) - critical density and temperature of argon ; b_j – the equation coefficients; $\gamma_j = 0$ for $j \leq 16$ and $\gamma_j = 1$ for $j \geq 17$.

In the work a structure (i.e. set of functions $\exp(\gamma_j\, \omega^{q_j})\, \omega^{r_j}/\tau^{t_j}$) and the coefficients $\{b_j\}$ of equation (1) were determinedby treatment both thermal and caloric experimental data. The equation of state was compiled in two stages. At the first stage, by a linear least square method, the joint functional Φ, including pvT data, data on isohoric specific heat and Maxwell criterion, was minimized:

$$\hat{O} = \sum_{k=1}^{n_1} W_k\, [\, A_0^e - A_0^c(\omega_k, \tau_k)]^2 + \sum_{k=1}^{n_2} W_k\, [\, C_{V_k}^e - C_V^c(\omega_k, \tau_k)]^2 +$$

$$+ \sum_{k=1}^{n_3} W_k\, \{\ln(\omega_k'/\omega_k'') + p_k\,(\rho_k'^{-1} - \rho_k''^{-1})/R/T_k - (f_k^{c\prime} - f_k^{c\prime\prime})\}^2 \qquad (2)$$

where n_1 - number of an experimental pvT data in single-phase region; n_2 - number of experimental data on isohoric specific heat; n_3 -number of experimental data at saturation line;$\{\rho'\}_k$ and $\{\rho''\}_k$ -values for saturated liquid and vapor density; W_k - weight of experimental data; indexes "c"and "e" refer, accordingly, to calculated and experimental values.

During minimization of a functional (2) the preliminarystructure and the equation coefficients were obtained by an addition- exception method [1].

At the second stage, the fundamental equation structure andequation coefficients were corrected. All selected data wereused for optimization, namely, the data on isobaric specific heatand velosity of sound were added also. The nonlinear least square method was used for minimizing the fuctional (3):

$$\hat{O} = \sum_{l}\sum_{k} W_{lk}\, [\, y_{lk}^e - y_{lk}^c]^2 + \sum_{s}\sum_{k} W_{sk}\, [\, y_{sk}^e - y_{sk}^c]^2 \qquad (3)$$

where the first part of a functional refers to the single-phase region, and the second to properties values at saturation line; y_l^c-property value calculated by equation (1); values y_l^e were calculatedunder condition of Maxwell criteria validity.

The covariance matrix, taking into account random errors, was determined during minimization of a functional (3). Then thefundamental equation assesment was carried out respect to both data, used for equation developing, and data unused before. For this purpose, the sliding examination method was

used [1]. The covariance matrixesfor systematic and computing errors was determined by a method of mathematical experiment. The total error matrix was also calculated. On the basis of equation (1), the density values at the given p and T were calculated from equation (4)

$$\pi = \omega\tau(1+ A_o) / z_c \qquad (4)$$

$$A_o = \sum_{j=1}^{32} (r_j - \gamma_j q_j \omega^{q_j}) b_j \exp(-\gamma_j \omega^{q_j}) \omega^{r_j} / \tau^{t_j} \qquad (5)$$

The other properties were calculated by usingdifferential relataions of thermodynamic

4. VISCOSITY AND THERMAL CONDUCTIVITY

The viscosity equation is defined as

$$\eta = \eta_o \cdot \exp(\Delta\eta) \qquad (6)$$

where η_0 and $\Delta\eta$ - the viscosity of rarefied gas and excessviscosity, respectively, are determined as follows:

$$\eta_o = \sum_{i=-3}^{3} a_i * \tau^{i/2} \qquad (7)$$

$$\Delta\eta = \sum_{j=1}^{18} c_i \omega^{r_j} / \tau^{t_j} \qquad (8)$$

The recommended thermal conductivity equation has the following form:

$$\lambda = \lambda_o + \Delta\lambda + \Delta\lambda_c \qquad (9)$$

where λ_0 , $\Delta\lambda$, $\Delta\lambda_c$ - the thermal conductivity of rarefied gas, theregular part of excess thermal conductivity, the separate scalingpart of excess thermal conductivity (this part is substantial onlyin the vicinity of the critical point), respectively, aredetermined as follows:

$$\lambda_o = \sum_{i=-4}^{5} a_i * \tau^{i/2} \qquad (10)$$

$$\Delta\lambda = \sum_{j=1}^{14} d_i \omega^{r_j} / \tau^{t_j} \qquad (11)$$

$$\Delta\lambda_c = d_{15} \omega^{0,5} / [\tau^* + 0,9 (\omega^*)^{1/0,35}]^{0,5} \qquad (12)$$

where $\tau^* = |\tau - 1|$, $\omega^* = |\omega - 1|$

Methods of obtaining of each of component in (6) and (9) are in whole coincide with the recommendations [2].

The equations of viscosity and thermal conductivity of a rarefied argon were obtained by approximating Standard Reference Data on viscosity and thermal conductivity at atmospheric pressure [48], which were reduced to zero density with use of second virial coefficient for η and λ [49] and densities at p = 0,101325 MPa, calculated with the obtained fundamental equation. Expressions (7) and (10) fitted the data on η and λ in the region of temperatures from the triple point up to 1500 K with mean square deviation 0,025 % and 0,016 %, accordingly. An error of values η and λ, evaluated in [48] as 0,5 %, was taken into account during of obtaining the equations for $\Delta\eta$ and $\Delta\lambda$, and also with an evaluation of errors of calculated values of viscosity and thermal conductivity. Structure of the equation (8) and the values of coefficients c_i are obtained by method, described in [2], on the basis of experimental data. The data weights were calculated with use the relative error of data. Realistic matrix of errors, taking into account random and probable systematic errors in data was also calculated during of approximating. On the basis of this matrix the relative errors data calculated on the equation (8) were evaluated.

Residual part of thermal conductivity (11) was calculated together here with part (12). This operation is possible because of application of expression on the basis of the simplified scale theory, when the unknown parameter enters linearly into the equation (12). Structure of the equation (11) and the values of coefficients d_i are obtained by method, described in [2], on the basis of experimental data. Realistic matrix of errors, taking into account random and probable systematic errors in data was also calculated during of approximating.

5. ASSESMENT OF REABILITY OF EQUATIONS

According to [2], the confidence limit for the estimated value of any property A is calculated as

$$\Delta A = \pm t_s (\mathbf{r}^T \mathbf{G}\, \mathbf{r})^{0,5} \qquad (13)$$

where t_s - the selected Student criterion for the confidence probability P = 0.95; **G** = **M** + **Q** + **B** - the generalized error matrix; **M** , **Q** è **B** - the error matrices for random, systematic and computing errors, respectively; **r** - the vector of the thermophysical function derivatives respect to the coefficients **b** of calculating equation ; the symbol "T" refers to the transposed vector.

According to (13), the errors of tabulated values of properties of argon were calculated and represented as relative errors $\delta À = 100 \Delta À/À$, % in Ref. [1]. (Computing errors were neglected because of their smallness).

The reability of the tabulated values of thermophysical properties can be established also on the basis of analysis of results of direct comparison of analytical results and experimental data. The results of such an analysis for thermodynamic properties are presented in last column of Tables 1.

The experimental data on velosity of sound [5,6,12] at saturation line did not used for the fundamental equation developing. The mean square deviation for these data in the temperature region 83.81-149.19 K is equal to 0.78 % for w' and 1.34 % for w".

As it is seen from Table 1, fundamental equation is adequate to experimental data, and the deviations do not exceed experimental data errors.

The analysis of the equations for viscosity and thermal conductivity shows, that both equations, and their coefficients are much significant, they represent experimental data with an adequate accuracy. In all cases (except data [27] on viscosity and [43] on thermal conductivity) mean square deviation does not exceed appreciated error of data. The summarized mean square deviation for whole file of viscosity data is equal to 1.25 %, and for thermal conductivity also 1.25%.

Statistical analysis of the viscosity and thermal conductivity equations shows, that the distribution of weighted residuals is close to normal. The final analysis of equation adequacy was carried out by the sliding examination method [2]. It is stated for residual viscosities and thermal conductivities, that the evaluated values of a dispersion differ from input values unsignificantly, that is convincing confirmation reability of models.

REFERENCES

1. A.D. Kozlov, V.M. Kuznetsov, Yu.V. Mamonov, M.D. Rogovin et al.

Argon in Liquid and Gaseous State. Thermodynamical Properties, Dynamic Viscosity and Thermal Conductivity at Temperatures 85 ... 1300 K and Pressures 0.1 ... 1000 MPa. Tables of Standard Reference Data GSSSD 179-96//Gosstandart of Russian: VNITsSMV. Deposited in VNITsSMV 5.01.97, No. 771-kk97.

2. A.D. Kozlov, V.M. Kuznetsov, Yu.V. Mamonov. The Analysis ofModern Methods of Development of Recommended Reference Dataon Viscosity and Thermal Conductivity of Gases and Liquids. The Reviews on Thermophysical Properties of Substances /TheThermophysical Center - Moscow: High Temperature Institute ofthe Academie of Sciences of USSR, 1989, part 3(77).

3. R.B. Stewart, R.T. Jacobsen. J. Phys. Chem. Ref. Data. 18:639 (1989).

4. A. Michels, J.M. Levelt, W. De Graaff. Physica 24:659 (1958)

5. W. Van Dael et al., Physica 32:611 (1966).

6. C.C. Lim, R.A. Aziz, Can. J. Phys. 45:1275 (1967).

7. K. Goldman, N.G. Scrase, Physica 45:1 (1969).

8. W.B. Streett, L.A.K. Staveley, J. Chem. Phys. 50(6):2302 (1969).

9. M.J. Terry et al., J. Chem. Thermod., (1):413 (1969).

10. O.B. Verbeke et al., J. Phys. Chem., 73(12):4076 (1969).

11. C. Gladun, Cryogenics,11:205 (1971).

12. J. Thoen, E. Vangeel, W. Van Dael, Physica 52:205 (1971).

13. A. Michels, Hub. Wijker, Hk. Wijker, Physica 15(7):627 (1949).

14. A. Lecocq, J. Des Recherches du C. N. R. S. (50):55 (1960).

15. E.R. Dobbs, L.J. Finegold, J. Acoustical Society of America 32(10):1215 (1960).

16. S.L. Robertson, S.E. Babb, G.J.Scott, J. Chem. Phys. 50(5): 2160 (1969).

17. J. Thoen, E.Vangeel, W. Van Dael, Physica 45:339 (1969).

18. H. Gielen, V. Jansoone V., O. Verbeke, J. Chem. Phys. 59(11): 5763 (1973).

19. W.B. Streett, M.S. Costantino, Physica 75:283 (1974).

20. M.A. Anisimov et al., Thermophysical Properties of Substances (8):237 (1975) (in Russian).

21. M. Nunes da Ponte et al., J. Chem. Thermod. 13(8):767 (1981).

22. S.F. Barrelros et al., J. Phys. Chem. 86(9):1722 (1982).

23. H.M. Roder H.M., R.A. Perkins, C.A. Nieto de Castro, Int. J. Thermophys. 10(6):1141 (1989).

24. M. Baba et al., Indian J. Technology, 30:553 (1992).

25. B.A. Younglove, H.J.M. Hanley, J. Phys. Chem. Ref. Data, 15(4):1323 (1986).

26. A. Michels, A. Botzen, W. Schuurman, Physica, 20:1141 (1954).

27. J.Kestin, Physica, 29:335 (1963).

28. J.P.Boon, Physica, 29:208 (1963).

29. J.A.Gracki, G.P.Flynn, J. Ross, J. Chem. Phys., 51(9):3856 (1969).

30. J. Kestin, E. Paykoc, J.V. Sengers, Physica, 54:1 (1971).

31. Termophysical Properties of Neon, Argon, Kripton, and Xenon. Ed. by V.A. Rabinovich (Moscow, Standard Publishing House, 1976), 636 p.

32. J. Vermesse, C.R. Acad. Sc. Paris, 277(B):191.

33. V.P. Slyusar', N.S. Rudenko, V.M. Tret^yakov, Thermophysical Properties of Substances, (7):50 (1973) (in Russian).

34. N.J. Trappeniers, P.S. Van der Gulik, Chem. Phys. Lett., 70(3):438 (1980).

35. S.V. Skorodumov, Development of the Capillare ViscosimeterTechnique, Experimental Study and Tabuliring Viscosity Values of Argon, Neon, and Helium at Temperatures 10-1300 K and Pressures 0.1-100 MPa. Author's Abstract oof Candidate Thesis (Moscow, Mosc. Power Institute, 1984).

36. H. Ziebland. et al., British J. Applied Physics, 9:52 (1958).

37. A. Michels, J.V. Sengers, L.J.M. Van de Klundert, Physica, 29:149 (1963).

38. B. Le Neindre. Et al., Proc. of the 8th Conference on Thermal Conductivity, (Plenum, N.Y.,1969), p. 75.

39. Kh.I. Amirkhanov, A.P. Adamov, G.D. Gasanov, IFG, 22(5):835 (1972) (in Russian).

40. J. Kestin et al., Physica, 100A:349 (1980).

41. C.A.N. DeCastro, H.M. Roder, J. Res. NBS 86(3):293 (1981).

42. A.A. Clifford et al., J. Chem. Soc. Faraday Trans. 1, 77:2679 (1981).

43. E.N. Haran et al., Ber. Bunsenges. Phys. Chem., 87:657 (1983).

44. A.I. Johns et al., J.Chem. Soc. Faraday Trans. 1, 82:2235 (1986).

45. U.V. Mardolcar, C.A.N. de Castro, W.A. Wakeham, Int. J. Thermophys., 7(2):259 (1986).

46. H.M. Roder, C.A.N. de Castro, U.V. Mardolcar, Int. J. Thermophys., 8(5):521 (1987).

47. J.C.G. Calado et al., Physica 143A:314 (1987).

48. Helium, Neon, Argon, Kripton, Xenon. Dynamic Viscosity andThermal Conductivity at Atmospheric Pressure (0.101325 MPA) in the Region of Temperature from Normal Boiling Points up to 5000 K. Tables of Standard Reference Data GSSSD 138-89 (Moscow, Standard Publishing House, 1992), 23 p.

49. J.C. Rainwater, D.G. Friend, Phys. Rev., A36, 36(8):4062 (1987).

Table I. Data on thermodynamic properties of an argon used for fundamental equation developing

Year	Reference	Property	Phase	Temperature, K	Pressure, ÌPà	Number of points	Standard deviation,, %
1949	[13]	ρ	fl	273...423	1.9...292.7	350	0.02
1958	[4]	ρ	g; l	118...248	0.6...104.2	290	0.07
1960	[14]	ρ	fl	573...1223	2.1...93.3	126	0.16
1969	[8]	υ	l	101...143	0.7...68.9	135	0.21
1969	[10]	υ	l; fl	87...202	0.2...15.2	275	0.28
1969	[16]	ρ	fl	308...673	119...1013	284	0.05
1973	[18]	υ	l; fl	149...153	4.6...5.3	20	0.93
1981	[21]	υ	l	110...120	1.3...137.6	96	0.20
1982	[22]	υ	l	129...147	5.6...142.2	72	0.30
1969	[7]	ρ′		87...145	---	36	0.08
1969	[9]	υ′		86...118	---	16	0.21
1989	[3]	ρ′		84...144	---	61	0.17
1989	[3]	p		84...144	---	61	0.07
1989	[3]	Â(Ò)		84...1100	---	49	2.4
1960	[15]	w	l	87...90	0.1...13.7	42	0.56
1969	[17]	w	l	100...150	0.3...51.6	174	0.36
1989	[3]	ρ″		84...144	---	61	0.29

Table I – Continued –

Year	Reference	Property	Phase	Temperature, K	Pressure, ÌPà	Number of points	Standard deviation,, %
1971	[12]	w	g; l; fl	121...169	0.3...6.9	189	0.80
1974	[19]	w	l; fl	90...160	0.1...340	229	0.25
1971	[11]	c_υ	l	88...151	-		
1975	[20]	c_υ	fl	151...263	-	151	1.3
1992	[24]	c_p	fl	323...423	5.0...21	33	1.3

ρ – density; v – specific volume; B(T) – the second virial coefficient; w – velocity of sound; c_v – isochoric specific heat; c_p – isobaric specific heat; p_s – pressure of saturated vapor, g – gas; l – liquid; fl – fluid.