

# **Automated System for Calculating Thermophysical Properties of Natural and Ozone-Safe Refrigerants and Their Mixtures**

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**ABSTRACT**

An automated system for calculating the thermophysical properties of monatomic and diatomic gases, air, carbon dioxide, water and steam, ammonia, some hydrocarbons, refrigerants and their mixtures has been created. It allows the calculation of compressibility factor, density, entropy, enthalpy, isochoric and isobaric specific heats, speed of sound, Joule-Thomson coefficient, viscosity, thermal conductivity, and some other properties. These parameters can be determined in the single-phase and two-phase regions and on the phase-equilibrium lines at temperatures from the triple point up to 400–1500 K and at pressures up to 70 or 100 MPa (in most cases). Properties can be calculated for the following twelve combinations of independent variables:  $T, \rho$ ;  $T, v$ ;  $T, p$ ;  $T, s$ ;  $T, h$ ;  $T, x$ ;  $p, \rho$ ;  $p, v$ ;  $p, s$ ;  $p, h$ ;  $p, x$ ;  $h, s$ .

**KEY WORDS:** automated system; gases; liquids; mixtures; thermophysical properties.

## 1. INTRODUCTION

For designing and investigation of cryogenic and refrigerating plants reliable data on thermophysical properties of working substances in wide region of parameters is necessary. For solving many practical tasks these data should be presented at different independent variables at various values of these variables. At present time automated systems are created, for example [1 – 4], which allow to obtain thermophysical properties of substances operatively by means of equations of state and equations for transport properties.

Because of the expansion of refrigerants' nomenclature and increased interest to the perspective mixtures of nature and ozone-safe refrigerants we created an automated system, which provide the calculation of thermodynamic and transport properties of monatomic and diatomic gases, air, carbon dioxide, water and steam, ammonia, some hydrocarbons, and other technically important substances.

## 2. AUTOMATED SYSTEM

### 2.1. General Description

The automated system provides users with data for nearly 30 technically important gases and liquids: monatomic gases (argon, neon, krypton, xenon, helium), diatomic gases (hydrogen, nitrogen, oxygen), air, carbon dioxide, water and steam, ammonia, some hydrocarbons (methane, ethane, ethylene, propane, n-butane), ozone-safe refrigerants (difluoromethane R-32, pentafluoroethane R-125, 1,1,1,2-tetrafluoroethane R-134a, 1,1,1-trifluoroethane R-143a) and some mixtures (R-32/R-125, R-32/R-134a, R-125/R-134a, R-125/R-143a, R-125/R-290, R-134a/R-290, R-134a/R-143a). Properties are calculated by setting of values of two independent variables for one-phase region and of one independent variable (temperature or pressure) for calculating properties on saturated or melting line. Properties may be calculated on one of two variants: "Single" (at given values of independent parameters), and "Interval" (at changing of temperature or pressure value in determined interval with certain step). Set of thermophysical properties and their units of measurement may be chosen according to certain task. The system provides work on two languages: English and Russian.

External view of working window is presented on Fig. 1. It consists of main menu string, working panels, information panel and resulting table. Calculated properties may be saving as the text file or electronic table MS Excel. On Fig. 2 the working window together with the windows for choosing of independent variables and for setting their values are presented.

For calculating thermodynamic properties of substances, most often unified equations of state in polynomial and fundamental forms are used. In some cases, for greater reliability, two forms of equation of state can be applied, and users have the option to choose either of them. The dependences of viscosity and thermal conductivity on temperature and density are used for calculation of transport properties.

The coefficients of the equations of state and the equations for the transport properties are stored for each substance. Parameters of the critical point and coefficients of equations for the ideal-gas functions, the saturated vapor pressure, and the melting pressure are also stored. For the majority of substances, reliable equations of state were employed that describe the experimental data on properties with high accuracy. Most of these equations were used for calculating tables of reference data.

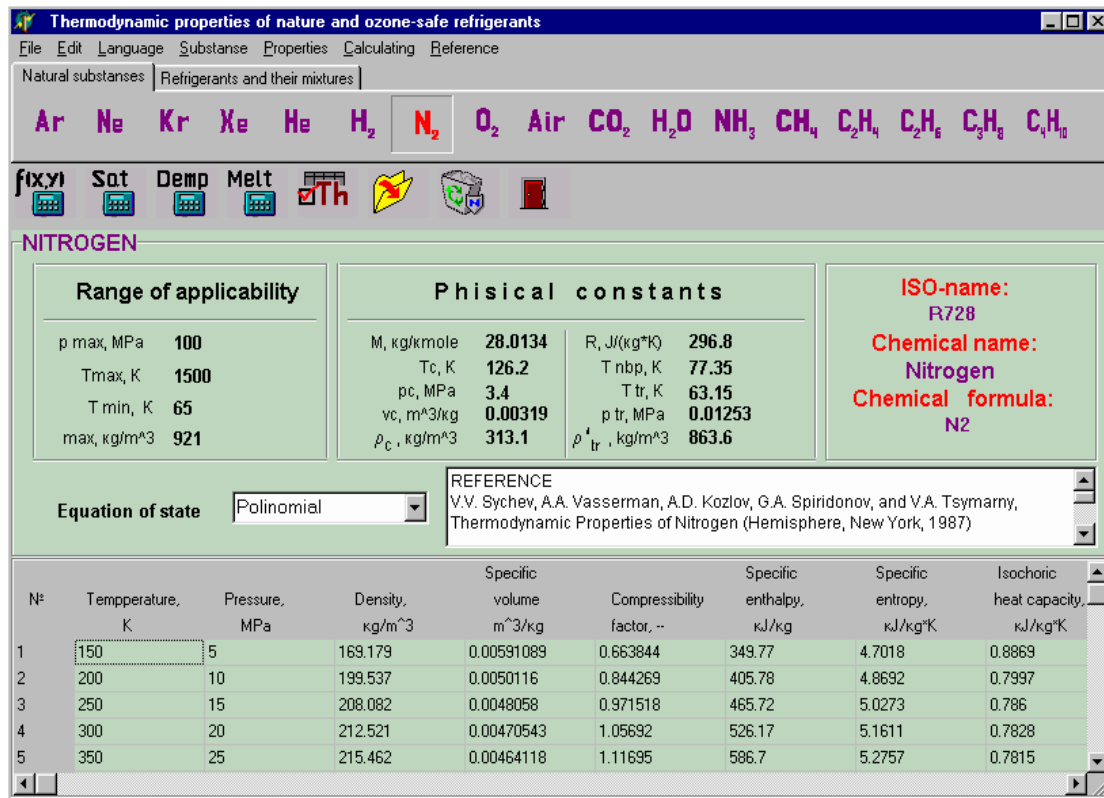


Fig. 1. Working window with calculated values of properties of Nitrogen.

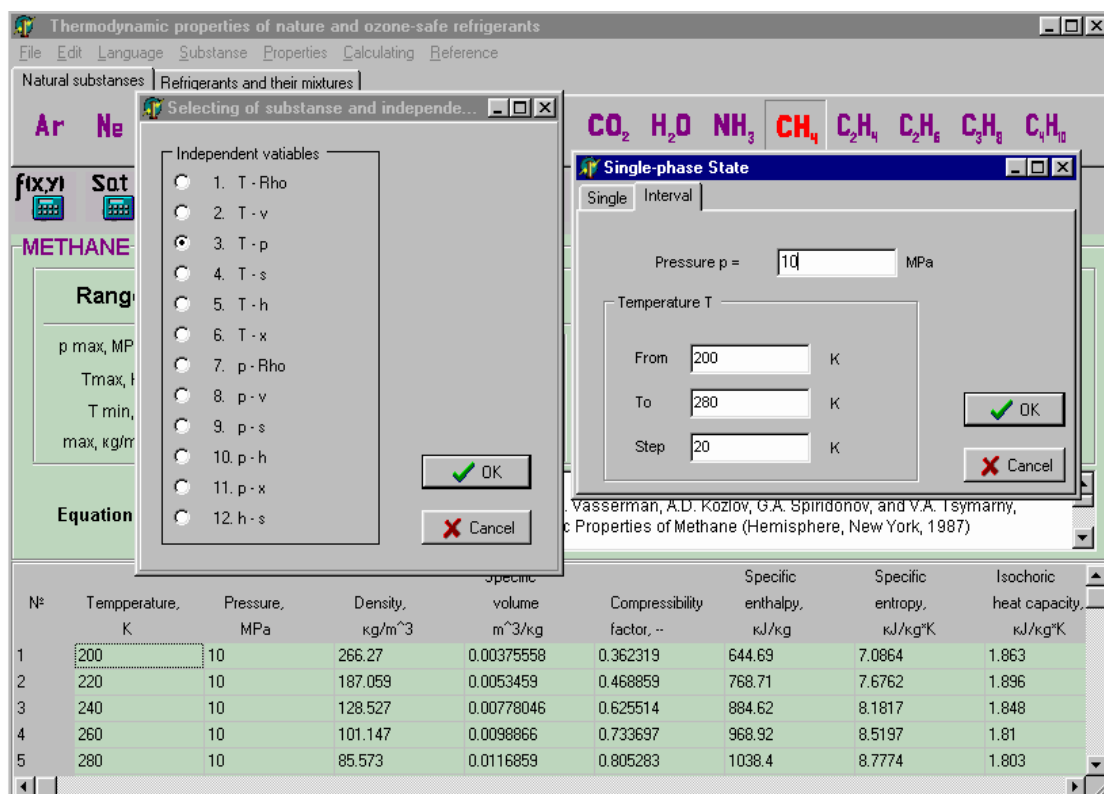


Fig. 2. Working window and windows for choosing of independent variables and for setting their values with calculated values of properties of Methane.

The system ensure the calculation of compressibility factor, specific volume, density, enthalpy, internal energy, entropy, isochoric and isobaric specific heats, speed of sound, Joule-Thomson coefficient, adiabatic exponent, volume expansion coefficient, thermal pressure coefficient, saturated vapor pressure, heat of vaporization, dynamic and kinematic viscosities, thermal conductivity, temperature conductivity and Prandtl number. The values of properties can be determined in the single-phase region, on the phase-equilibrium lines and in the two-phase region at temperatures from the triple point up to 400 – 1500 K and at pressures up to 70–100 MPa (for some substances - up to higher or lower pressures). More detail information on the regions of parameters is given in the next paragraph.

## 2.2. Used Equations

Equations of state in two forms – polynomial and fundamental – were used in the system for calculating thermodynamic properties. We used, in most cases, the equation of state having a polynomial form, which is convenient for fast calculation of various properties,

$$z = 1 + \sum_{i=1}^m \sum_{j=0}^{s_i} b_{ij} \frac{\omega^i}{\tau^j}, \quad (1)$$

where  $z = p/(\rho RT)$  is the compressibility factor,  $b_{ij}$  is the coefficients of equation,  $\omega = \rho/\rho_{cr}$  – is the reduced density,  $\tau = T/T_{cr}$  – is the reduced temperature;  $T$ ,  $p$ ,  $\rho$ ,  $R$  are respectively temperature, pressure, density, and gas constant; the subscript “cr” indicates the properties in the critical point.

In spite of the simplicity of form these equations of state [6,7,12,15,18,20,24,27–30,32] ensure a quite accept accuracy of thermodynamic properties calculating.

For many substances, so-called fundamental equations of state are also used. These equations have the form:

$$\alpha(\omega, \tau) = \frac{A(\rho, T)}{RT} = \alpha^0(\omega, \tau) + \alpha^r(\omega, \tau), \quad (2)$$

where  $A(\rho, T)/(RT)$  is the dimensionless Helmholtz energy,  $\alpha^0$  is the ideal-gas part of  $\alpha$ , and  $\alpha^r$  is the real part of  $\alpha$ .

The function  $\alpha^0$  is calculated on the basis of data on ideal-gas isobaric specific heat and is approximated by the relation from  $\tau$ . The function  $\alpha^r$  may be represented in the form

$$\alpha^r(\omega, \tau) = \sum_{i=1}^m \sum_{j=0}^{s_i} b_{ij} \frac{\omega^i}{\tau^j} + \exp(-\gamma\omega^2) \sum_{i=1}^n \sum_{j=1}^{r_i} c_{ij} \frac{\omega^i}{\tau^j}, \quad (3)$$

where  $b_{ij}$ ,  $c_{ij}$ ,  $\gamma$  are coefficients of equation.

In some cases the function  $\alpha^r$  is represented in a more complicated form containing different powers of  $\omega$  in the exponential terms.

The fundamental equations [5,9,11,13,16,19,21–23,26,31,33–35] provide a higher accuracy in the critical region then polynomial. The advantage of Eq. (2) is the possibility for calculating all thermodynamic properties only by differentiation of the function  $\alpha(\omega, \tau)$ . Both polynomial and fundamental equations allow the calculation of thermodynamic properties in one-phase region and on saturation line because the Maxwell’s rule was taken into account at their compiling.

The equations describing the data for viscosity and thermal conductivity and data on ideal-gas functions and on saturated vapor pressure and melting pressure have different forms for various substances. This circumstance was taken into account in the development of the programs for the automated system. Finally, the system was constructed with the use of equations of state of the form of Eq. (1) or (2), in the vast majority of cases, and various forms of equations, describing the transport properties, ideal-gas functions, and data on the saturation line.

Equations of state, which are used in this system, provide the calculation of gas and liquid density at pressures to 10 MPa and temperatures to 400 K with uncertainties of  $\pm 0,05$  %, and at higher values of these parameters with uncertainties of  $\pm 0,1$  %. The uncertainty of calculated values of enthalpy are not higher than 0.5 and 1.5 kJ/kg respectively, and of specific heat – 0.5 and 2.0 %. In the critical region the uncertainty may be higher on 2–3 times than maximal of pointed values.

The literature sources from which the equations for calculation of thermodynamic and transport properties were taken are given in table 1. In this table, the intervals of temperature and maximum values of density and pressure for each equation are also indicated.

### 2.3. Calculation of Properties

At designing of refrigerating and cryogenic plants the thermophysical properties are calculated repeatedly at different combinations of independent variables. The calculated values of properties must be reliable and agree among themselves on all points of thermodynamic surface by different combinations of independent parameters. The accuracy was ensured by use of reliable equations of state and equations for calculating transport properties for each substance, and also by setting of small values of admitted uncertainties in the iteration cycles.

In the creation of automated system great attention was paid to the compiling of program for calculating the thermophysical properties using various combinations of independent variables, but not only as a function of temperature and pressure. Properties can also be calculated for the following twelve combinations of independent variables: temperature – density ( $T - \rho$ ), temperature – specific volume ( $T - v$ ), temperature – pressure ( $T - p$ ), temperature – enthalpy ( $T - h$ ), temperature – entropy ( $T - s$ ), temperature – quality ( $T - x$ ), pressure – density ( $p - \rho$ ), pressure – specific volume ( $p - v$ ), pressure – enthalpy ( $p - h$ ), pressure – entropy ( $p - s$ ), pressure – quality ( $p - x$ ), enthalpy – entropy ( $h - s$ ).

The problem of calculating thermophysical properties for different independent variables arises because, in equation of state, the density and temperature have a degree more than three. Therefore it is necessary to use iterative methods for determining the values of these parameters.

For calculating properties for coordinates  $T - x$  and  $p - x$  and also for coordinates  $T - \rho$  and  $T - v$  at temperatures lower than critical, the properties on saturation line are first calculated. It is necessary (in coordinates  $T - \rho$  and  $T - v$ ) for finding-out the phase state in which the substance is located at given parameters. The necessary values of pressure (or temperature) and densities of the saturated vapor and liquid are calculated in the first approach by means of auxiliary equations, and then by means of the unified equation of state on the base of Maxwell's rule.

**Table I.** List of Substances, Sources of Equations and Intervals of Parameters

Substances	Sources of equations		Temperature range $\Delta T$ , K	Max. density ( $\text{kg}\cdot\text{m}^{-3}$ )	Max. pressure (MPa)
	For thermal properties	For transport properties			
Argon	[5]	[6]	84–700	1830	1000
Helium	[7]		2–1500	300	100
		[8]	2–1000	300	100
	[9]		2.2–1500	307	100
Krypton	[10]	[6]	120–1300	2570	100
Neon	[11]		25–700	1248	700
Xenon	[6]	[6]	161–1300	3100	100
Hydrogen	[11]		14–500	85	40
Nitrogen	[12]		65–1500	920	100
	[13]		63–1000	1600	2200
		[14]	65–1000	920	200
Oxygen	[15]		55–1500	1350	100
	[16]		55–300	1340	80
		[17]	70–500	1340	100
Air	[18]		70–1500	1020	100
Carbon dioxide	[19]		216–1100	1450	800
Water and steam	[20]		273–1073	1220	1000
	[21]		252–1273	2150	25000
	[22]		251–1273	1400	1000
Ammonia	[23]		195–700	850	1000
Methane	[24]		91–1000	480	100
	[25]		91–625	580	1000
		[26]	91–1000	480	100
Ethylene	[27]		110–600	700	300
Ethane	[28]		91–700	660	80
Propane	[29]		100–700	720	100
<i>n</i> -Butane	[30]		135–700	750	100
Difluoromethane (R-32)	[31]		180–500	1380	70
	[32]		180–500	1380	70
Pentafluoroethane (R-125)	[31]		180–500	1761	70
	[32]		180–500	1761	70
Tetrafluoroethane (R-134a)	[33]		170–455	1552	70
Trifluoroethane (R-143a)	[33]		161–433	1276	35
R-32/R-125	[33]		200–440	1475	35
R-32/R-134a	[33]		200–440	1484	35
R-125/R-134a	[33]		200–413	1604	35
R-125/R-143a	[33]		200–413	1441	35
R-125/R-290	[34]		253–423	1150	7
R-134a/R-290	[35]		255–400	1100	6
R-134a/R-143a	[33]		243–413	1431	17

For calculating the properties in coordinates  $T - p$ ,  $T - h$ , and  $T - s$ , it is necessary first to determine the third parameter used in the equation of state (and in equations for transport properties), the density. To determine the density from equation of state one of two iteration methods (Newton's method or method of bisection) is used. The density in coordinates  $T - h$  is determined taking into account the fact, that on many isotherms for given value of enthalpy two corresponding values of density exist. After the number of iterations a good agreement of preset value of pressure, enthalpy or entropy with the value defined by equation of state is achieved.

For calculating the properties for coordinates  $p - v$  and  $p - \rho$  it is first necessary to determine the temperature. The temperature is determined by iteration on the given isochore by the method of bisection. After that one can define all the properties on corresponding algorithm in accordance with the phase state of substance.

For coordinates  $p - h$  and  $p - s$ , both the independent variables of the equation of state, temperature and density, must be determined. For their calculating double iterative cycle is employed. First the temperature is determined by iteration on the isobar on the basis of known thermodynamic relations. And then the value of density necessary for calculation of caloric properties ( $h$  or  $s$ ) is determined for a given pressure. The iterative calculations for determining  $T$  and  $\rho$  are repeated until admissible errors of density, enthalpy, and entropy are reached.

At calculating the properties in the coordinates  $h - s$  neither of the three thermal parameters connected with the equation of state is given. Therefore, the algorithm for calculation of thermophysical properties in this coordinates is based on a relative comparison of given and calculated values of enthalpy on the given isentrope.

To ensure the agreement of the values of thermodynamic properties which are calculated in different coordinate systems, the following values of admissible errors were applied: for pressure and density – 0.001 %, for temperature – 0.0001 K, for enthalpy – 0.05 J/mol, and for entropy – 0.005 J/(mol·K).

The software of the automated system, having a modular structure, permits an increase in the number of substances, calculated properties, and independent variables. The program is intended for work under the handle of operating systems Windows 98/2000/NT/Me/XP. At installation to hard drive it occupies 1.3 Mbytes.

### 3. CONCLUSIONS

Calculations carried out by means of the automated system confirm the internal agreement of the properties' values, which were defined at different combinations of independent variables. The information possibilities of developed system are rather higher than possibilities of published tables of reference data.

The program software of the system allows to increase the number of calculated properties and combinations of independent variables and also to fill up the system by equations for calculating properties of new substances.



## REFERENCES

1. R. Krauss, K. Stephan, A.I. Johns et al, Data Banks and Prediction Packages.//Transport Properties of Fluids: Their Correlation, Prediction and Estimation. – Cambridge: University Press, 1996. – 483 p.
2. M.J. Skovrup, A. Jacobsen, B.D. Rasmussen, S.E. Andersen, CoolPack, A Collection of Simulation Tools for Refrigeration – Version 1.46, Technical University of Denmark, Department of Mechanical Engineering, Lyngby, Denmark, 2000.
3. A.A. Vasserman, S.V. Bodyul Automated System for Calculating Thermophysical Properties of Air and its Components, *Technicheskie Gazy*, №3, p.p.4 – 9 (2001).
4. Lemmon E.W., McLinden M.O., and Huber M.L. REFPROP, Thermodynamic and Transport Properties of Refrigerants and Refrigerant Mixtures. Standard Reference Database 23 –Version 7.0, NIST: U.S. Secretary of Commerce on behalf of the United States of America, 2002.
5. Ch. Tegeler, R. Span, and W. Wagner, *J. Phys. Chem. Ref. Data* **28** (2): 779 – 850 (1999).
6. V.A. Rabinovich, A.A. Vasserman, V.I. Nedostup, and L.S. Veksler, *Thermophysical Properties of Neon, Argon, Krypton and Xenon* (Hemisphere, New York, 1987) (originally published by Standards Publ. House, Moscow, 1976).
7. V.V. Sychev, A.A. Vasserman, A.D. Kozlov, G.A. Spiridonov, and V.A. Tsymarny, *Thermodynamic Properties of Helium* (Hemisphere, New York, 1987) (originally published by Standards Publ. House, Moscow, 1984).
8. A.D. Kozlov, V.M. Kuznetsov, Yu.V. Mamonov, A.A. Aleksandrov, A.B. Matvev, V.I. Sukhov, A.F. Arinin, and S.F. Serov, *Tables of Standard Reference Data. Helium-4. Dynamic Viscosity and Thermal Conductivity at Temperatures from 2,2 to 1000 K and Pressures from Corresponding to Rarefied Gas to 100 MPa. GSSSD 92–86* (Standards Publ. House, Moscow, 1986).
9. R.D. McCarty, and V.D. Arp, A New Wide Range Equation of State for Helium, *Adv. Cryogen. Engin.* **35**: 1465-1475 (1990).
10. V.V. Altunin, V.A. Rabinovich, and M.A. Sakhabetdinov, *Tables of Standard Reference Data. Liquid and Gaseous Krypton. Density, Enthalpy, Entropy, Isobaric Specific Heat and Velocity of Sound in the Temperature Range 120 to 1300 K and the Pressure Range 0.1 to 100 MPa. GSSSD 95-86* (Standards Publ. House, Moscow, 1986).
11. S.G. Penoncello, R.T. Jacobsen, E.W. Lemmon, *Thermodynamic Properties of Cryogenic Fluids* (Kluwer Academic Publishers 1997).
12. V.V. Sychev, A.A. Vasserman, A.D. Kozlov, G.A. Spiridonov, and V.A. Tsymarny, *Thermodynamic Properties of Nitrogen* (Hemisphere, New York, 1987) (originally published by Standards, Moscow, 1977).
13. R. Span, E.W. Lemmon, R.T. Jacobsen, and W. Wagner, A Reference Quality Equation of State for Nitrogen, *Int. J. of Thermophys.* **19**: 1121 – 1132 (1998).
14. A.D. Kozlov, V.M. Kuznetsov, Yu.V. Mamonov, M.G. Stepanova, V.I. Sukhov, A..F. Arinin, and S.F. Serov, *Tables of Standard Reference Data. Nitrogen. Dynamic Viscosity and Thermal Conductivity at Temperatures from 65 to 1000 K and Pressures from Corresponding to Rarefied Gas State to 200 MPa. GSSSD 89–85* (Standards Publ. House, Moscow, 1986).

15. V.V. Sychev, A.A. Vasserman, A.D. Kozlov, G.A. Spiridonov, and V.A. Tsymarny, *Thermodynamic Properties of Oxygen* (Hemisphere, New York, 1987) (originally published by Standards, Moscow, 1981).
16. R.B. Stewart, R.T. Jacobsen, W. Wagner, Thermodynamic Properties of Oxygen from the Triple Point to 300 K with Pressures to 80 MPa, *J. Phys. Chem. Ref. Data* **20**(5): 917-948 (1991).
17. A.D. Kozlov, V.M. Kuznetsov, Yu.V. Mamonov, V.I. Sukhov, A.F. Arinin, and S.F. Serov, *Tables of Standard Reference Data. Oxygen. Dynamic Viscosity and Thermal Conductivity at Temperatures from 70 to 500 K and Pressures from Corresponding to Rarefied Gas to 100 MPa. GSSSD 93–86* (Standards Publ. House, Moscow, 1986).
18. V.V. Sychev, A.A. Vasserman, A.D. Kozlov, G.A. Spiridonov, and V.A. Tsymarny, *Thermodynamic Properties of Air* (Hemisphere, New York, 1987) (originally published by Standards, Moscow, 1978).
19. R. Span, and W. Wagner, A New Equation of State for Carbon Dioxide, *J. Phys. Chem. Ref. Data* **25** (6) (1996).
20. V.V. Sychev, A.A. Vasserman, A.Ya. Kreyzerova, and V.A. Tsymarny, in *Properties of Water and Steam. Proceedings of the 11<sup>th</sup> Int. Conf. Edited by M. Pichal and O. Sifner* (Hemisphere, New York, 1989), pp. 40–47.
21. A. Saul, and W. Wagner, A Fundamental Equation for Water Covering the Range from the Melting Line to 1273 K at Pressures up to 25000 MPa, *J. Phys. Chem. Ref. Data* **18** (4): 1537-1564 (1989).
22. A.Pruss, and W.Wagner, A New Equation for Water as a Candidate for New Scientific Formulation of IAPWS, *Physical Chemistry of Aqueous Systems: Meeting the Needs of Industry. Proceedings of the 12th International Conference on The Properties of Water and Steam* (1995).
23. R. Tillner-Roth, F. Harms-Watzenberg, H.D. Baehr, Eine neue Fundamentalgleichung fuer Ammoniak, *DKV-Tagungsbericht. 20 Jahrgang , Nurnberg*, pp. 166-181 (1993).
24. V.V. Sychev, A.A. Vasserman, A.D. Kozlov, G.A. Spiridonov, and V.A. Tsymarny, *Thermodynamic Properties of Methane* (Hemisphere, New York, 1987) (originally published by Standards, Moscow, 1979).
25. A.D. Kozlov, V.M. Kuznetsov, Yu.V. Mamonov, V.I. Sukhov, A.F. Arinin, *Tables of Standard Reference Data. Methane. Dynamic Viscosity and Thermal Conductivity at Temperatures from 91 to 1000 K and Pressures from Corresponding to Rarefied Gas to 100 MPa. GSSSD 94–86* (Standards Publ. House, Moscow, 1986).
26. U. Zetzmann, and W. Wagner, A New Equation of State and Tables of Thermodynamic Properties of Methane Covering the Range from the Melting Line to 625 K at Pressures up to 1000 MPa, *J. Phys. Chem. Ref. Data* **20**(6) (1991).
27. V.V. Sychev, A.A. Vasserman, A.D. Kozlov, G.A. Spiridonov, and V.A. Tsymarny, *Thermodynamic Properties of Ethane* (Hemisphere, New York, 1987) (originally published by Standards, Moscow, 1982).
28. V.V. Sychev, A.A. Vasserman, A.D. Kozlov, G.A. Spiridonov, and V.A. Tsymarny, *Thermodynamic Properties of Ethylene* (Hemisphere, New York, 1987) (originally published by Standards, Moscow, 1981).
29. V.V. Sychev, A.A. Vasserman, A.D. Kozlov, and V.A. Tsymarny, *Thermodynamic Properties of Propane*. (Hemisphere, New York, 1990) (originally published by Standards Publ. House, Moscow, 1989).

30. V.V. Sychev, A.A. Vasserman, A.D. Kozlov, and V.A. Tsymarny, *Thermodynamic properties of butane* (Begell House inc., New York, 1995).
31. A.A. Vasserman, D.V. Fominsky, Equations of State for Ozone-Safe Refrigerants R-32 and R-125, *Int. J. Thermophys.* **22** (4): 1089–1098 (2001).
32. A.A. Vasserman, A.V. Bogdanov, D.V. Fominsky, The Unified Equations of State in the Polynomial Form for Refrigerants of R-32 and R-125, *Technicheskie Gazy* № 1 (2002).
33. R. Tillner-Roth, A. Yokozeki, H. Sato, and K. Watanabe, *Thermodynamic Properties of Pure and Blended Hydrofluorocarbon (HFC) Refrigerants* (Japan Society of Refrigerating and Air Conditioning Engineers, Tokyo, 1998).
34. A.A. Vasserman, V.P. Malchevsky, The Equation of State for mixture of refrigerants R-125/R-290, *Cholodilnaya Technika i Technologiya* № 1 (2006).
35. A.A. Vasserman, V.P. Malchevsky, The Equation of State for mixture of refrigerants R-134a/R-290, *Problemy tehniki* № 1 (2006).