International Journal of Thermophysics, Vol. 15, No. 6, 1994

Thermophysical Property Standard Reference Data from NIST[1]

D. G. Friend[2,3] and M. L. Huber[2]

The National Institute of Standards and Technology (NIST) has a primary function to develop and disseminate standard reference data for the thermophysical properties of fluids and fluid mixtures of interest to the industrial and scientific communities. In this paper we discuss five computerized databases distributed by the Standard Reference Data (SRD) Program of NIST. The databases provide national standards for the properties of pure fluids, an accurate evaluated mixture program focusing on the properties of natural gas mixtures, a predictive package emphasizing hydrocarbon systems up to C_{20}, a database for refrigerant and prospective alternative refrigerant fluids, and the current scientific thermophysical property surfaces for pure water and steam. The databases include both thermodynamic surfaces and representations for transport properties over broad ranges of temperature, pressure, and composition. We also discuss our current research to improve the standards for air and for aqueous systems including the binary mixture of ammonia and water.

KEY WORDS: databases; mixtures; predictive models; refrigerants; standards; thermodynamic properties; transport properties.

1. INTRODUCTION

The National Institute of Standards and Technology (NIST; formerly the National Bureau of Standards; NBS) plays a key role in the basic infrastructure for the development and transfer of technology of interest to the nation's industrial and commercial sectors. Within the area of thermophysical properties of fluids, the Thermophysics Division of NIST has a long history in the areas of measurement, evaluation, and correlation for

[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

[2] Thermophysics Division, National Institute of Standards and Technology, Boulder, Colorado 80303, U.S.A.

[3] To whom correspondence should be addressed.

0195-928X/94/1100-1279$07.00/0

well-characterized and important fluid systems. The Standard Reference Data Program (SRD) of NIST distributes much of the standard reference data established as part of this effort in the form of computerized databases. These standards are used throughout the chemical and related industries as the basis of custody transfer, as well as for process design, innovation, and optimization.

In the manuscript we first discuss each of the five computer databases under active development and currently supported within the Division, thus providing an update of an earlier publication on computer packages [1]. Then we discuss our efforts toward the development of standard thermophysical property surfaces for air and for aqueous systems.

2. PURE FLUIDS DATABASE

The current NIST standards for pure fluids are incorporated into the NIST Thermophysical Properties of Pure Fluids Database (NIST12, formerly MIPROPS) [2]. The fluids present in the NIST12 database are listed in Table I; for each of these fluids, the thermodynamic surface is based on a highly accurate 32-term modified Benedict–Webb–Rubin (MBWR) equation of state. For most of the fluids, correlations are also provided for viscosity, thermal conductivity, and dielectric constant. A separate program for helium covers both the superfluid and the normal fluid states and uses a different form for the thermodynamic surface; additional properties for the superfluid state, including superfluid fraction and second- and fourth-sound coefficients, can also be calculated. (The main program in the database can calculate properties of helium over a more restricted range which excludes the superfluid region.) Typical uncertainties of these standards are about 0.1–0.3% in density, 0.5–2% in enthalpy, 2–5% in heat capacities, 2% in viscosity, and 4–6% in thermal conductivity over a broad range of the state variables. The references cited in the

Table I. Component Database in NIST12 and NIST14

Argon	Isobutane	*n*-Butane	Deuterium[a]
Carbon dioxide	Carbon monoxide	Ethane	Ethylene
Helium[a]	Normal hydrogen[a]	Parahydrogen[a]	Methane
Nitrogen trifluoride[a]	Oxygen	Propane	Nitrogen
Xenon[a]	*n*-Hexane[b]	Isohexane[b]	*n*-Pentane[b]
Isopentane[b]	*n*-Heptane[b]	Hydrogen sulfide[b]	

[a] Available in NIST12 only.
[b] Available in NIST14 only.

Table II. Properties Computed by NIST12

Pressure[a]	Temperature[a]	Density[a]
Volume[a]	Enthalpy[a]	Entropy[a]
Energy[a]	Quality[a]	PV/RT
Latent heat	C_p	C_v
$\gamma = C_p/C_v$	Expansivity	Gruneisen parameter
Isothermal compressibility	Sound speed	JT coefficient
Thermal conductivity	Viscosity	Prandtl No.
Diffusivity	Dielectric constant	

[a] Can also be used as optional input variable; the melting line and saturation properties can also be specified on input.

user's manual provided with the database give more detailed information about the accuracy of the correlations in various regions of the phase diagram [1].

The interactive program is menu-driven and user-friendly; short help messages and informative error messages are provided. The user has a wide choice of units for each of the input and output properties: SI units, customary engineering units, chemical units, etc. Output comprises one to seven columns of thermophysical properties specified by the user; it is written to the screen as well as to a file. The choices of properties are shown in Table II. The input state variable can be entered from the keyboard or from a file specified by the user. The state point at which properties are calculated is specified by a pair of parameters selected as indicated in Table II. An input parameter can be used in an iterative mode: an initial, incremental, and final value can be given and a resultant table of properties generated. Additional fluids are being added to future versions of the NIST12 database.

3. PROPERTIES OF WATER

The specialized water database [3] represents the current scientific formulation for the fluid phases of this substance as adopted by the International Association for the Properties of Water and Steam (IAPWS) [4] and can be used as the basis of property calculations associated with processes using steam as the working fluid. The interactive program for pure water substance covers a very wide range of temperatures and pressures: it reproduces experimental data within their accuracy for pressures up to 1000 MPa and for temperatures from 0 to 1000°C and is designed to extrapolate well up to 2000°C and 2000 MPa.

The formulation is in the form of a Helmholtz function of temperature and density so that all equilibrium properties can be obtained directly from

combinations of this function and its derivatives. The database program can provide 16 equilibrium properties in addition to the viscosity and thermal conductivity [5]. The units for input and display can be chosen by the user, and calculations can be made at a single point or a table can be produced. Single points can be chosen by specifying pairs of the independent variables temperature (T), pressure (p), density (ρ), entropy (S), and enthalpy (H): (T, p), (T, ρ), (T, S), (T, H), (p, S), (p, H), or the coexisting liquid and vapor properties at a specified temperature or pressure. Tables of isothermal, isobaric, isochoric, and saturation properties can be obtained.

We anticipate that IAPWS will adopt a new thermodynamic surface in the near future, based on a new correlation representing the most recent data and which uses the ITS-90 temperature scale. This surface will replace the current NIST SRD database as appropriate.

4. MIXTURE PROPERTY DATABASE

The most accurate standard thermophysical property surfaces for mixtures are described by the NIST Mixture Property Database (NIST14; formerly called DDMIX) [6] which provides properties of the pure fluids listed in Table I and their mixtures for temperatures to 1000 K and pressures to 300 MPa. The emphasis of this database is on accurate density calculations (especially for CO_2-rich natural gas mixtures [7]), but it provides excellent results for other properties and mixtures as well. The program provides the following properties: density, C_p/C_v, C_p, enthalpy, entropy, molecular mass, sound speed, Joule–Thomson coefficient, viscosity, and thermal conductivity.

The database uses an extended-corresponding states algorithm with "exact" shape factors [8] determined from accurate thermodynamic surfaces for each of the pure components. Thus, the pure fluid limits reduce to the standards of the NIST12 database [2]. The program also performs several common phase-equilibrium calculations, such as bubble-point and dew-point temperatures and pressures, using a Peng–Robinson formulation. There is an extensive help feature, a units menu, table options, and optional file-based input and output.

Typical uncertainties in the density of the pure components are within 0.1–0.3% (except in the critical region where errors can be much larger). For mixture computations, the uncertainties in the densities are generally within less than 1% for hydrocarbon systems [7]. This database has become widely accepted in the petroleum, gas, and petrochemical industries.

5. PREDICTION OF FLUID PROPERTIES

The NIST Thermophysical Properties of Hydrocarbon Mixtures Database (SUPERTRAPP) [9] emphasizes prediction of thermophysical properties for a large number of fluid systems which have not been adequately measured to establish standard property surfaces. The interactive program

Table III. Component Database in SUPERTRAPP

Methane	*n*-Octane	1-Hexene
Ethane	2,3,3,4-Tetramethylpentane	1-Heptene
Propane	2,2,4,4-Tetramethylpentane	1-Octene
n-Butane	2,2,3,4-Tetramethylpentane	1-Nonene
Isobutane	2,2,3,3-Tetramethylpentane	1-Decene
n-Pentane	2,2,5-Trimethylhexane	Propadiene
Isopentane	2,2-Dimethylheptane	1,3-Butadiene
Neopentane	2-Methyloctane	1,2-Butadiene
2,2-Dimethylbutane	*n*-Nonane	Cyclopropane
2,3-Dimethylbutane	2,2,5,5-Tetramethylhexane	Cyclopentane
3-Methylpentane	2,2,3,3-Tetramethylhexane	Methylcyclopentane
2-Methylpentane	3,3,5-Trimethylheptane	Ethylcyclopentane
n-Hexane	*n*-Decane	Cyclohexane
2,2,3-Trimethylbutane	*n*-Undecane	Methylcyclohexane
3,3-Dimethylpentane	*n*-Dodecane	Ethylcyclohexane
2,4-Dimethylpentane	*n*-Tridecane	Benzene
2,3-Dimethylpentane	*n*-Tetradecane	Toluene
2,2-Dimethylpentane	*n*-Pentadecane	Ethylbenzene
3-Ethylpentane	*n*-Hexadecane	*o*-Xylene
3-Methylhexane	*n*-Heptadecane	*m*-Xylene
2-Methylhexane	*n*-Octadecane	*p*-Xylene
n-Heptane	*n*-Nonadecane	Propylbenzene
2,2,3,3-Tetramethylbutane	*n*-Eicosane	Isopropylbenzene
2,3,4-Trimethylpentane	*n*-Heneicosane	Butylbenzene
2,3,3-Trimethylpentane	*n*-Docosane	Isobutylbenzene
2,2,4-Trimethylpentane	*n*-Tricosane	*t*-Butylbenzene
2,2,3-Trimethylpentane	*n*-Tetracosane	Naphthalene
3-Methyl-3-ethylpentane	Ethylene	1-Methylnaphthalene
2-Methyl-3-ethylpentane	Propylene	2-Methylnaphthalene
3,4-Dimethylhexane	2-Methylpropene	Biphenyl
3,3-Dimethylhexane	*cis*-2-Butene	Hydrogen
2,5-Dimethylhexane	*trans*-2-Butene	Nitrogen
2,4-Dimethylhexane	1-Butene	Oxygen
2,3-Dimethylhexane	2-Methyl-2-butene	Water
2,2-Dimethylhexane	2-Methyl-1-butene	Carbon monoxide
3-Ethylhexane	3-Methyl-1-butene	Carbon dioxide
4-Methylheptane	*cis*-2-Pentene	Sulfur dioxide
3-Methylheptane	*trans*-2-Pentene	Hydrogen sulfide
2-Methylheptane	1-Pentene	

allows calculations for the 116 pure fluids listed in Table III and mixtures of up to 20 components for temperatures to 1000 K and pressures to 300 MPa. The program also allows the user to introduce a new component into the database with minimal information. Its predictive technique is based on extended corresponding states with shape factors estimated from generalized relationships [10].

Phase equilibrium problems (bubble- and dew-point pressures, flashes) are solved using the Peng–Robinson equation of state, and the user may obtain the thermodynamic properties by using either the extended corresponding-states method or the Peng–Robinson equation. The program provides the following properties: density, C_p/C_v, C_p, enthalpy, entropy, molecular mass, sound speed, Joule–Thomson coefficient, viscosity, and thermal conductivity. As in the NIST14 database, a units menu, help feature, tabular options, and file-based input and output are designed to assist the user.

The extended corresponding-states method is a very powerful technique that computes predictions for an unknown fluid system by performing a scaling operation on a reference fluid (propane, in this database) whose properties are very well known. For pure fluids, the corresponding-states prediction has associated uncertainties of better than 2% in compressed liquid densities and 5–8% for liquid viscosity and thermal conductivity. For mixtures, liquid densities are typically estimated within 3%, and liquid viscosity and thermal conductivity to 5–10%. Although the predictive calculations are somewhat more uncertain than the more typical standard reference thermophysical property surfaces, the large database and ability to add new fluids ensure its importance in the SRD program.

6. REFRIGERANTS AND REFRIGERANT MIXTURES

The environmental concerns associated with CFC refrigeration fluids have led to an expansive program of measurement and modeling to identify alternatives and to very active development of the REFPROP database [11]. This interactive program calculates thermodynamic and transport properties of refrigerants and mixtures of refrigerants of up to five components as listed in Table IV. The range of applicability is approximately $0.5T_c$ to $2T_c$ with pressures to about $2.2P_c$, where the subscript refers to the value at the critical point.

The user has a choice of models for the equilibrium properties of the pure fluids. The available models are (1) the Carnahan–Starling–DeSantis (CSD) equation of state [12], (2) an extended corresponding-states model [13] similar to that used in the SUPERTRAPP database discussed above, and (3) an accurate standard reference thermodynamic surface for the 11

Table IV. Component Database in REFPROP

R11	R114	R143	Cyclopropane
R12	R115	R143a	Perfluoropropane
R13	R123[a]	R152a	Carbon dioxide[a,b]
R13B1	R123a[b]	R218	*n*-Butane[a,b]
R14	R124[a]	E134	*i*-Butane[a,b]
R21	R125[a]	E245[b]	*n*-Pentane[a,b]
R22	R134	R227ea[b]	*i*-Pentane[a,b]
R23	R134a[a]	R236ea[b]	Ammonia[a,b]
R32[a,b]	R141b	R245cb[b]	
R113	R142b	Propane[a]	

[a] Standard reference thermodynamic surface available.
[b] New to Version 4.

fluids indicated in Table IV. The transport properties (viscosity and thermal conductivity) are found from the extended corresponding-states method [14]. For mixtures of the pure components, interaction parameters have been measured for about 65 pairs. For those pairs for which a measured interaction parameter is not available, a very successful algorithm [15] is used to predict the interaction parameter.

The user may choose up to seven of the following variables to display at any given time: T, P, V, ρ, S, H, C_v, C_p, sound speed, dP/dT, dP/dV, $dP/d\rho$, viscosity, and thermal conductivity. A variety of calculations is also available: isotherms, isobars, isochores, isenthalps, isentropes, 2-phase with P increment, and 2-phase with T increment. One also may choose the units, the reference state for enthalpy and entropy, an informational screen for pure fluids (displaying such informaton as the normal boiling point, critical parameters, molecular mass, dipole moments and polarizability, and estimates of the surface tension), or a table option. Tables may be calculated for fixed values of temperature, pressure, density, entropy, or enthalpy. Tables of dew-point and bubble-point properties may also be obtained along isotherms or isobars. The tables may be stored in a file designated by the user.

This program is updated periodically with new fluids as data become available, with revised parameters for existing fluids, and with new features as they are developed. The package as supplied also contains the Fortran source language for the package of subroutines and a demonstration main program showing the use of the subroutines for users who would like to incorporate the calculations into their own programs. This database has become a primary calculational tool in industries associated with refrigeration, and NIST remains very active in the further development of domestic and international standards in this area.

7. STANDARDS UNDER DEVELOPMENT

The standards discussed above are available from the SRD office of NIST in the form of computer programs. Research in the Division toward the development of additional standard thermophysical property surfaces of current interest to industry is ongoing. As these projects are completed, some additions and refinements will be made in the existing computerized databases, and new specialized databases will be made available for distribution. A project on the thermophysical properties of standard air and related mixtures of nitrogen, oxygen, and argon is nearing completion. This research, sponsored mainly by the National Aero-Space Plane project within NASA [16], included experimental measurements primarily at NIST and modeling work performed primarily at the Center for Applied Thermodynamic Studies at the University of Idaho [17]. The work pointed to problems in the previous standards for air, especially at low temperatures, and has already proven to be of great use in more traditional aspects of the aerospace industry.

Interest in aqueous systems is long-standing because of the ubiquitous nature of this solvent, because of its presence in petroleum reservoirs and pipelines, and, most recently, because of the interest in supercritical water reactors and in binary working fluids for the power industry. Recent formulations have been completed for water + carbon dioxide mixtures [18] and for water + nitrogen [19]. These formulations were based on an extended corresponding-states model with the IAPWS formulation for water as the reference system [3] and empirical shape factors to correlate the mixture properties. Very recently [20], we have examined the data for these systems with the exact-shape-factor model of the NIST14 computerized database [6].

The system ammonia + water is being used as a working fluid in a pilot plant for electric power generation [21], and more widespread use is anticipated. Although several thermophysical property surfaces are available for this system, there are inconsistencies in the data and in the correlating formulations. A program of experimental and modeling work to establish standard reference thermophysical property surfaces for this system is under way in the Division. More than 5000 experimental data are available in the literature, and the process of data evaluation is under way. The extended corresponding-states algorithm of NIST14 [6] is being used for this system, with the pure fluids represented by the IAPWS formulation for water [3] and the Haar–Gallagher surface for ammonia [22]. Phase equilibrium in the critical region is also being examined using scaling theories.

8. CONCLUSION

Standards have long been recognized as vital in the commercial and industrial sectors, no less so in the area of thermophysical properties of fluids as in the more basic standards of time, length, mass, and temperature. The Thermophysics Division of NIST and the Fluid Properties Data Center within the Division have a primary mission to establish and provide such standards. Although data may be available from many sources, including proprietary data from industrial laboratories, and correlations are available from a variety of vendors, the necessity of impartial standards has led to the strong program within NIST. These standards represent carefully evaluated property data with resultant extremely accurate correlating surfaces, although there is some compromise associated with the smooth representations over large ranges of independent variables, with the simplicity and speed of the computational code and, most importantly, with the long-term stability of the NIST standard thermophysical property surfaces disseminated by the Standard Reference Data Program. The computerized databases have achieved broad acceptance in a variety of industrial applications for process control, simulation, design, and optimization as well as for standards associated with custody transfer. The increasing trend toward international commerce and the increasingly stringent requirements for technological data will lead to continual improvements and extensions of the standard databases available from NIST.

ACKNOWLEDGMENT

We gratefully acknowledge partial financial support from the Standard Reference Data program at NIST.

REFERENCES

1. D. G. Friend, M. L. Huber, and J. S. Gallagher, in *Computerized Thermophysical Property Packages, HTD-Vol. 225*, S. G. Penoncello, ed, ASME Winter Ann. Mtg. (1992), p. 13.
2. *NIST Thermophysical Properties of Pure Fluids Database*, NIST12, Version 3.0 (Natl. Inst. Stand. Technol., Gaithersburg, MD, 1992).
3. *NIST Thermophysical Properties of Water Database*, SRD 10 (Natl. Inst. Stand. Technol., Gaithersburg, MD, 1985).
4. L. Haar, J. S. Gallagher, and G. S. Kell, *NBS/NRC Steam Tables* (Hemisphere, New York, 1984).
5. J. V. Sengers and B. Kamgar-Parsi, *J. Phys. Chem. Ref. Data* 13:185 (1984); Int. Assoc. Prop. Steam, *Release on Thermal Conductivity of Water Substance* (1975).
6. *NIST Mixture Property Program*, NIST14, Version 9.08 (Natl. Inst. Stand. Technol., Gaithersburg, MD, 1992).

7. G. J. Sherman, J. W. Magee, and J. F. Ely, *Int. J. Thermophys.* **10**:47 (1989).
8. J. F. Ely, *Adv. Cryo. Eng.* **35**:1511 (1990).
9. *NIST Thermophysical Properties of Hydrocarbon Mixtures Database*, SUPERTRAPP, SRD 4, Version 1.04 (Natl. Inst. Stand. Technol., Gaithersburg, MD, 1990).
10. T. W. Leland, J. S. Rowlinson, and G. A. Sather, *Trans. Faraday Soc.* **64**:1447 (1968); J. F. Ely and H. J. Hanley, Nat. Bur. Stands. (U.S.) Technical Note 1039 (1991).
11. *NIST Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database*, REFPROP, Version 4.01 (Natl. Inst. Stand. Technol., Gaithersburg, MD, 1994).
12. G. Morrison and M. O. McLinden, Natl. Bur. Stands. (U.S.) Technical Note 1226 (1986).
13. M. L. Huber and J. F. Ely, *Int. J. Refrig.* **17**:18 (1994).
14. M. L. Huber and J. F. Ely, *Fluid Phase Equil.* **80**:239 (1992); M. L. Huber, D. G. Friend, and J. F. Ely, *Fluid Phase Equil.* **80**:249 (1992).
15. G. Morrison and M. O. McLinden, *Int. J. Refrig.* **16**:129 (1993).
16. R. T Jacobsen, S. G. Penoncello, S. W. Beyerlein, E. W. Lemmon, W. P. Clarke, J. C. Rainwater, J. F. Ely, D. G. Friend, and W. M. Haynes, NASP Tech. Mem. 1005, Suppl., REF WBS 2.3.04, Version 5.0 (1995), in press.
17. R. T Jacobsen, S. G. Penoncello, S. W. Beyerlein, W. P. Clarke, and E. W. Lemmon, *Fluid Phase Equil.* **79**:113 (1992).
18. J. S. Gallagher, R. Crovetto, and J. M. H. Levelt Sengers, *J. Phys. Chem. Ref. Data* **22**:431 (1993).
19. J. S. Gallagher, J. M. H. Levelt Sengers, I. M. Abdulagatov, J. T. R. Watson, and A. Fenghour, Natl. Inst. Stand. Technol. Technical Note 1404 (1993).
20. J. S. Gallagher, D. G. Friend, J. A. Given, and J. M. H. Levelt Sengers, *Int. J. Thermophys.*, in press.
21. C. H. Marston, *Mech. Eng.* **114**(9):76 (1992).
22. L. Haar and J. S. Gallagher, *J. Phys. Chem. Ref. Data* **7**:635 (1978).