THERMOPHYSICAL PROPERTY COMPUTER PACKAGES FROM NIST OF INTEREST TO THE NATURAL GAS INDUSTRY[1]

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ABSTRACT

We discuss three computerized databases distributed by the Standard Reference Data (SRD) program of NIST, which are of interest to the natural gas industry. The databases include national standards for the properties of pure fluids, an accurate evaluated mixture program, and a predictive package emphasizing hydrocarbon systems. The databases provide both thermodynamic surfaces and representations for transport properties over a broad range of temperature and pressure. We briefly describe the databases and discuss important features and capabilities. The mixture programs allow phase equilibria calculations such as dew and bubble-point pressure calculations and provide the thermophysical properties of each phase. Included in these properties are densities, heat capacities, sound speeds, enthalpies, entropies, viscosities and thermal conductivities. We present sample comparisons with experimental data for density in two multicomponent mixtures representative of natural gas systems in the United States, and a sample dew-point temperature calculation for a mixture containing methane, propane, and n-butane.

KEY WORDS: databases, density, mixtures, natural gas, predictive models, standards, thermophysical properties, transport properties, vapor-liquid equilibria.

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INTRODUCTION

The Physical and Chemical Properties Division of the National Institute of Standards and Technology (NIST) is active in the measurement, evaluation, and correlation of thermophysical properties for industrially important fluid systems. Much of the standard reference data obtained through NIST research is distributed by the Standard Reference Data (SRD) office of NIST [1] in the form of computerized databases. These reference formulations are used throughout the chemical and related industries as the basis of custody transfer as well as for process design, innovation and optimization. Currently the Division is active in supporting and developing a range of databases, covering a wide variety of systems including alternative refrigerants, air, steam, cryogens, ammonia/water and hydrocarbon systems.

In this paper we discuss three computerized databases that are available from NIST and are of specific interest to the natural gas industry. We describe their capabilities and give sample comparisons with experimental data. We then discuss the future direction of our research program involving natural gas mixtures. The first database we discuss is the NIST Thermophysical Properties of Pure Fluids Database [2] (also called NIST12, formerly MIPROPS). It is a pure fluid database that contains standard reference thermodynamic surfaces for 17 pure fluids. The second database is the NIST Mixture Property Database [3] (also called NIST14, v9.08, formerly called DDMIX). It is a mixture database containing typical components of natural gases, from methane to n-heptane, as well as nonhydrocarbons such as hydrogen sulfide, carbon dioxide and nitrogen. The final database we discuss is an estimation program, the NIST Thermophysical Properties of Hydrocarbon Mixtures Database [4] (NIST4, also called SUPERTRAPP).

DATABASES

Pure Fluids Database

The current NIST reference formulations for pure fluids are incorporated into the NIST12 Database [2]; these properties are often adopted as consensus standards by organizations such as ASTM [5]. The fluids present in this database are listed in Table 1 and include natural gas components such as methane, ethane, propane, iso- and n-butane. (Properties for several of these pure fluids are also available on the NIST Chemistry Webbook [6], which can be found on the Internet at http://webbook.nist.gov). Each of these fluids is represented by 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 normal fluid states using 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.) Typical uncertainties of these reference formulations 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 user's manual provided with the database give more detailed information about the accuracy of the correlations in various regions of the phase diagram.

Table 1. Component database in NIST12

methane	normal hydrogen	carbon dioxide	argon
ethane	parahydrogen	carbon monoxide	xenon
propane	deuterium	oxygen	nitrogen trifluoride
n-butane	helium	nitrogen	
i-butane			
ethylene			

The DOS-based, interactive database 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, engineering units, etc. Output comprises one to seven columns of thermophysical properties as specified by the user; it can be written to the screen as well as to a file. The choices of properties are shown in Table 2. The input state variables 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 from the choices given in Table 2. The second input parameter can be used in an iterative mode: an initial, incremental, and final value can be given and the resultant table of properties will be generated. Properties can also be calculated along the saturation (liquid and vapor) boundary.

Table 2. Properties computed by NIST12.

pressure[1]	temperature[1]	density[1]
volume[1]	enthalpy[1]	entropy[1]
energy[1]	quality[1]	PV/RT
latent heat	C_p	C_v
gamma[2]	expansivity	Gruneisen parameter
isothermal compressibility	sound speed	JT coefficient
thermal conductivity	viscosity	Prandtl number
diffusivity	dielectric constant	melting pressure

[1]Can also be used as optional input variable. [2]Ratio of heat capacities.

The pure fluid standard property surfaces contained in the NIST12 database are currently under review, and we anticipate a major upgrade of this database scheduled for 1999. Many of the 32-term BWR-type equations will be replaced by newer formulations with improved accuracy. For several of these new formulations, uncertainties in density are as low as 0.01 % in large regions of the phase diagram. In addition, the number of fluids will be increased and the database will include

hydrocarbons as heavy as n-octane. In Table 3, we give a list of fluids proposed as components in the next release of the pure fluid database. This future version will also incorporate a graphical user interface for ease of use in many interactive computational situations.

Table 3. Pure Fluid Standards under Revision and Development

methane	argon
ethane	nitrogen
propane	oxygen
n-butane	carbon monoxide
i-butane	carbon dioxide
n-pentane	hydrogen sulfide
i-pentane	helium
neopentane	hydrogen
n-hexane	parahydrogen
i-hexane	deuterium
n-heptane	sulfur hexafluoride
n-octane	nitrogen trifluoride
cyclohexane	neon
ethylene	krypton
propylene	xenon
methanol	fluorine
	ammonia

Mixture Property Database

Accurate thermophysical property surfaces for mixtures are provided by the NIST14 Database [3], which provides properties of the pure fluids, listed in Table 4, and their mixtures. The emphasis of this database is on accurate density calculations (especially for CO_2-rich mixtures [7]), but it provides excellent results for other properties and mixtures as well. The database computes several common phase equilibrium calculations, such as P, T flashes, and bubble and dew-point pressures and temperatures, and gives properties for the resulting phases. The program provides the following thermophysical properties: compressibility factors, 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. The interface also has an extensive help feature, a units menu, table options, and optional file-based input and output. Binary interaction parameters for mixture calculations are provided in the program; however the user may change the binary interaction parameters in order to optimize agreement with a specific data set.

Table 4. Component database in NIST14

methane	n-pentane	ethylene	hydrogen sulfide
ethane	i-pentane	nitrogen	carbon monoxide
propane	n-hexane	oxygen	carbon dioxide
n-butane	i-hexane	argon	
i-butane	n-heptane		

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) and for mixture computations, densities are within less than a percent for hydrocarbon-hydrocarbon systems and less than 0.6% for mixtures containing CO_2 [7]. This database has become widely accepted as a reference formulation in the petroleum, gas, and petrochemical industries.

Because of the importance of natural gas systems, NIST has been working on new models for mixture properties, which will be incorporated into future versions of the mixture database, NIST14. The updated version of NIST14 will have a graphical user interface and will incorporate a new mixture model based on an n-fluid residual Helmholtz formulation [9]. This model will also reduce to the reference formulations of NIST12 in the pure fluid limits. It contains mixture parameters developed using the most recent experimental data for natural gas systems. Typical uncertainties of calculated mixture properties are expected to be 0.2% in density and 1% in heat capacities for most calculations. In the region from 250 K to 350 K at pressures up to 30 MPa, uncertainties in densities are about 0.1% for most gaseous phase mixtures. For binary mixtures where the critical point temperatures of the pure fluid constituents are within 100 K of each other, the uncertainty of calculated bubble-point pressures will generally be within 1 to 2%; for mixtures with critical points further apart, the uncertainties will be 5 to 10%.

Prediction of Fluid Properties

The NIST4 Database [4] emphasizes prediction of thermophysical properties for a large number of fluid systems that have not been adequately measured to establish standard property surfaces. The interactive, DOS-based database allows calculations for the 192 pure fluids listed in Table 5 and their mixtures of up to 20 components. The fluids include hydrocarbons up to C_{24} as well as common impurities such as carbon dioxide, nitrogen, oxygen and hydrogen sulfide. The FORTRAN source code for property prediction is also included, so that a user may link it with other software. The predictive technique is based on extended corresponding states [10-12] and is designed primarily for nonpolar hydrocarbons.

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 to within 3 %, and liquid viscosity and thermal conductivity to 5-10 %. Although the predictive calculations are more uncertain than the more typical reference thermophysical property surfaces, the large number of fluids and the ability to add new fluids make it important to industry.

The database performs common phase equilibrium calculations such as isentropic (T, S), and isenthalpic (P, H) flashes, (T, P), and (T, D) flashes and can calculate bubble and dew-point temperatures and pressures. The feed composition must be specified upon input. 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. Phase equilibrium is determined with the Peng-Robinson equation of state, while the user may obtain the thermodynamic properties using either the extended corresponding states method or the Peng-Robinson equation. Binary interaction parameters are included in the program; the user may, however, enter alternative values of the binary interaction parameters to optimize the agreement with a particular data set. As in other NIST databases, a units menu, help feature, tabular options, and file-based input and output are designed to assist the user.

The database also has the useful feature that allows a user to introduce a new component into the database with a minimal amount of information, and save it. The minimum amount of information needed to introduce a new component is the molecular mass, the normal boiling point and the critical temperature, pressure and volume. In addition, the user may enter vapor pressures and saturated liquid densities to improve the predictions.

For example, methyl mercaptan is often used as an odorant in natural gas, but it is not in the list of fluids given in Table 5. At certain temperatures and pressures, some condensate may form in the natural gas. Since the odorant has a preference for the liquid phase, the concentration of the odorant in the gas is reduced, contributing to fading. This phenomenon may be modeled with the database by adding methyl mercaptan to the SUPERTRAPP library of components. Pure fluid parameters such as the critical temperature, pressure and volume, the normal boiling point, the molar mass, vapor pressures, and liquid densities are readily available [13]. The database prompts the user to supply this information, and stores it into the fluid library. Property predictions with the odorant and natural gas mixtures may then be performed.

SELECTED COMPARISONS WITH EXPERIMENTAL DATA

We compared the predictions of the NIST4 and NIST14 models with density data [14] for two natural gas mixtures representative of compositions of U.S.

commercial Gulf Coast (GC1) and Amarillo (AM1) gases. The mixtures were prepared gravimetrically with the compositions given in Table 6. The results of these comparisons

Table 5. Component database in NIST4

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
i-butane	2,2,3,3-tetramethylpentane	1-decene
n-pentane	2,2,5-trimethylhexane	propadiene
i-pentane	2,2-dimethylheptane	1,3-butadiene
neopentane	2-methyloctane	1,2-butadiene
2,2-dimethylbutane	n-nonane	cyclopropane
2,3-dimenthylbutane	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	ortho-xylene
3-methylhexane	n-heptadecane	meta-xylene
2-methylhexane	n-octadecane	para-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-methylnapthalene
2-methyl-3-ethylpentane	propylene	2-methylnapthalene
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[1]
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	

[1] Limited to less than 0.05 mole percent

Table 5. Component database in NIST4, continued

1,1-dimethylcyclopentane	trans-1,3-dimethylcyclopentane
trans-1,2-dimethylcyclopentane	1-trans,3-dimethylcyclohexane
tran-1,2-cis,4-trimethylcyclopentane	tran-1,2-cis,3-trimethylcyclopentane
1-cis,2-trans,4-trimethylcyclopentane	1-trans,4-dimethylcyclohexane
1,1-dimethylcyclohexane	1-cis,3-dimethylcyclohexane
1-methyl,trans-3-ethylcyclopentane	1-methyl,trans-2-ethylcyclopentane
1-methyl,cis-3-ethylcyclopentane	1-methyl-1-ethylcyclopentane
1-cis-2,cis-3-trimethylcyclopentane	isopropylcyclopentane
cis-1,2-dimethylcyclohexane	n-propylcyclopentane
1,1,3-trimethylcyclopentane	p-ethyltoluene
1,3,5-trimethylbutylbenzene	o-ethyltoluene
1,2,4-trimethylbenzene	1,1,4-trimethylcyclohexane
1-cis,3-cis-5-trimethylcyclohexane	1-cis,2-trans-4-trimethylcyclohexane
1,1,2-trimethylcyclohexane	1-cis,2-cis,4-trimethylcyclohexane
isobutylcyclopentane	2,3,5-trimethylhexane
4-methyloctane	2,4-dimethylheptane
2,5-dimethylheptane	3,5-dimethylheptane
3,3-dimethylheptane	2,3-dimethylheptane
3,4-dimethylheptane	1-methyl-3-isopropylbenzene
1-methyl-2-isopropylbenzene	1-methyl-3-propylbenzene
1-methyl-4-propylbenzene	1,2-diethylbenzene
1,4-diethylbenzene	1-methyl-2-propylbenzene
1,4-dimethyl-2-ethylbenzene	1,2-dimethyl-4-ethylbenzene
sec-butylbenzene	1,3-dimethyl-2-ethylbenzene
1,2-dimethyl-3-ethylbenzene	1,2,4,5-tetramethylbenzene
isobutylcyclohexane	n-butylcyclohexane
2,2-dimethyloctane	3,6-dimethyloctane
3,3-dimethyloctane	2,3-dimethyloctane
2-methylnonane	3-methylnonane
2-methylbutylbenzene	1-tert-butyl-2-methylbenzene
n-pentylbenzene	1-tert-butyl-3,5-dimethylbenzene
1,3,5-triethylbenzene	1,2,4-triethylbenzene
n-hexylbenzene	1-methyl,trans-2-(4-methylpentyl)cyclopentane
3-methyloctane	cis-1,4-dimethylcyclohexane
m-ethyltoluene	cis-1,3-dimethylcyclopentane
cyclopentadiene	cis-decalin
acetylene	trans-decalin
silane	argon

Table 6. Compositions of natural gas mixtures GC1 and AM1

Component	GC1 (mole fraction)	AM1 (mole fraction)
methane	0.96580	0.90644
ethane	0.01815	0.04553
n-propane	0.00405	0.00833
i-butane	0.00099	0.00100
n-butane	0.00102	0.00156
i-pentane	0.00047	0.00030
n-pentane	0.00032	0.00045
n-hexane	0.00063	0.00040
nitrogen	0.00269	0.03134
carbon dioxide	0.00589	0.00466

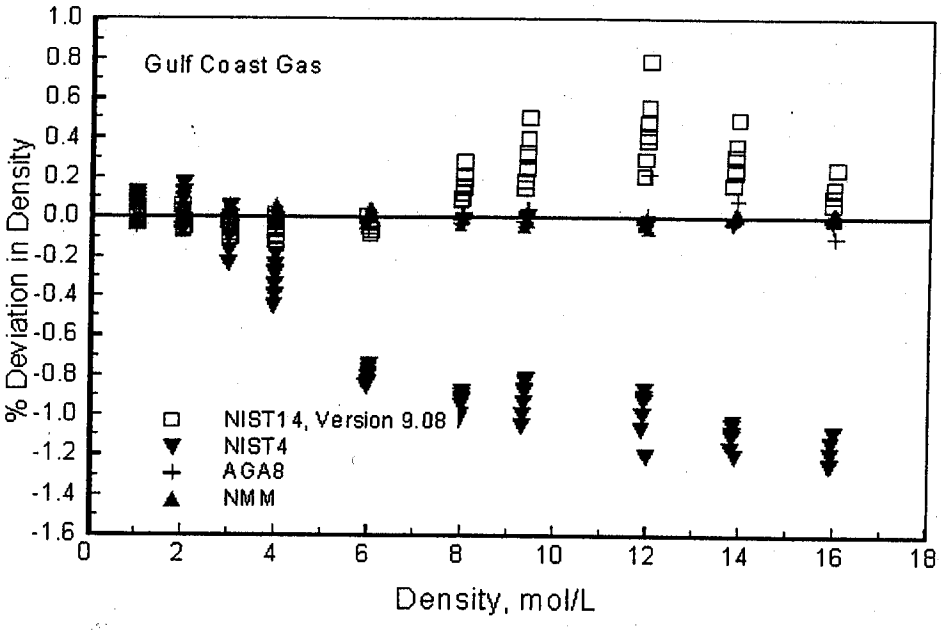

Figure 1. Density Comparisons for Gulf Coast Gas

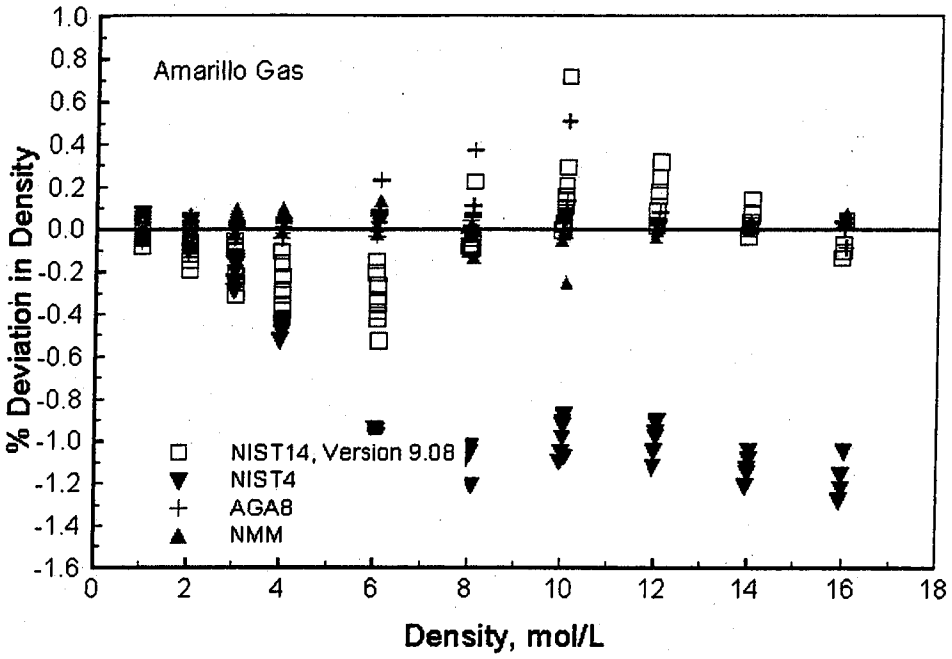

Figure 2. Density Comparisons for Amarillo Gas

are given in Figures 1 and 2. The figures show the results of the AGA-8 [15] model, the current NIST14 model (v9.08), the NIST4 prediction program, and a new mixture model (NMM) which is under development for future versions of NIST14. For the GC1 gas, both NMM and AGA-8 generally represent the experimental density data to within about a tenth of a percent. The highest deviations in density are for very low temperature (225 K), dense fluid points (12-16 mol/liter) which were not available for the development of the AGA-8 model and lie at the extremes of its intended usage range. The current NIST14 model gives slightly larger deviations, especially as the density increases above about 8 mol/L. It is also clear that the NIST4 prediction program is not as accurate as the other three models, which are reference surfaces. The results for the AM1 gas are similar, with the AGA-8 and NMM showing very good agreement with the experimental data, generally to within about a tenth of a percent. As mentioned earlier, the binary interaction parameters in the current NIST14 program may be modified to improve the representation of a specific data set. In this manner, the deviations shown in Figures 1 and 2 for the current NIST14 model can be substantially reduced.

Figure 3 shows a sample of dew-point temperature comparisons for a ternary mixture containing methane, propane and n-butane [16]. Comparisons are presented for the current NIST14 model and the prediction program NIST4. (AGA-8 is valid for the gas phase only and is not applicable here). Both programs give about the same results for the dew-point temperature calculations, which are within 3 % of the experimental

values. The temperature range of this data set is from 310 to 344 K, and the pressure range is from 6.8 to 11.7 MPa.

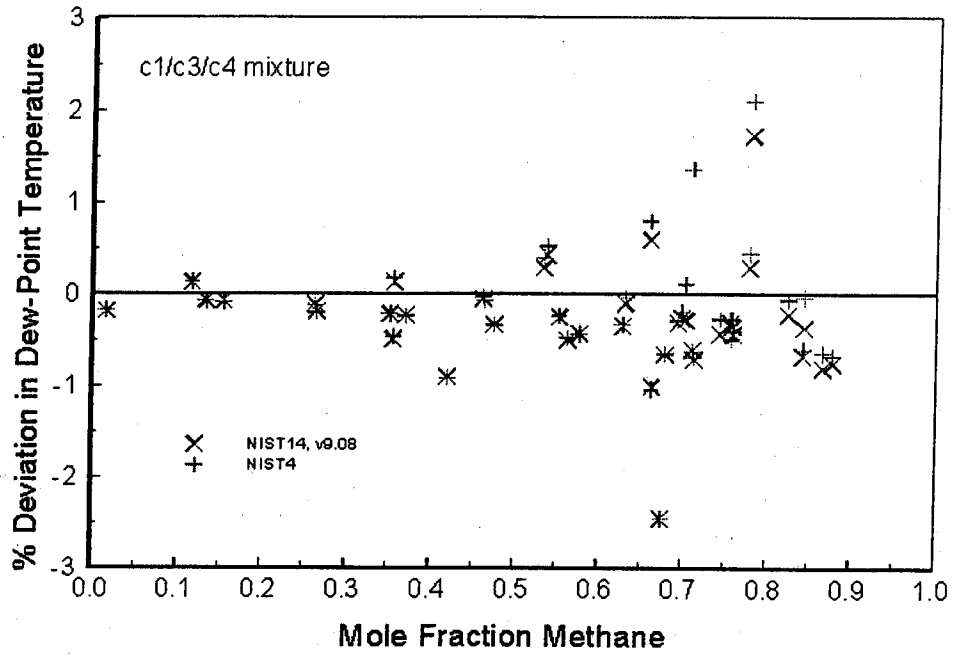

Figure 3. Dew-point temperature comparisons for a methane, propane, n-butane mixture

CONCLUSIONS

We have briefly described three interactive computer programs developed by the Physical and Chemical Properties Division of NIST which are of interest to the natural gas industry: NIST Thermophysical Properties of Pure Fluids Database (NIST12), NIST Mixture Property Database (NIST14) and NIST Thermophysical Properties of Hydrocarbon Mixtures (NIST4). These are an important part of the larger system of standard reference databases, which are available through NIST [1].

Although the natural gas industry is in many respects mature, it is also under intense competitive pressure and facing an array of technical challenges. The databases discussed in this paper represent one aspect of a continuing commitment by NIST to assist the industry in areas related to property data and measurements. In addition to making improvements in the accuracy, adding graphical user interfaces, and increasing the scope of the databases mentioned above, we are beginning a new project of focussed measurements. We also are becoming more active in national and international standardization of measurements and models, are expanding our concern with the effects of impurity species, and have initiated a project to study precipitates and solid-fluid

equilibrium problems of interest to the industry. As in the past, we anticipate a continuing goal of assisting the natural gas and related industries with the development of the required data infrastructure.

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