

# The History of NIST's Refrigerants Program:

## II. Thermophysical Properties Research

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### ABSTRACT

*The history of the research program on thermophysical properties of refrigerants at the National Institute of Standards and Technology (NIST) is described in this paper. The program has roots extending back to at least 1909. The current program began in 1981 as a collaboration between the Physical and Chemical Properties Division and the NIST Thermal Machinery Group to provide properties for the refrigerant mixtures being investigated for use in heat pumps. With the implication of the CFC refrigerants in the destruction of stratospheric ozone, the program increased dramatically in scope in 1987. The program includes experimental measurements and modeling of both the thermodynamic and transport properties of a wide variety of fluids and fluid mixtures; these results are transferred to industry in a variety of ways, including a computer database known as REFPROP. Because of its long-standing program in fluid properties, NIST was in a unique position to respond to the urgent international need for data on new refrigerants.*

### BACKGROUND

Thermophysical properties are essential data for the analysis of any process employing a working fluid. They are needed for the modeling of refrigeration cycles and for the conversion of raw data (temperatures, pressures, etc.) measured in machinery or heat-transfer tests to the desired quantities, such as compressor efficiency and Nusselt number. The thermodynamic properties include density, pressure, fugacity, internal energy, enthalpy, entropy, Gibbs and Helmholtz energies, heat capacities, speed of sound, chemical potential, and the Joule-Thomson coefficient, as well as phase equilibrium properties. They are distinguished from the trans-

port properties of viscosity, thermal conductivity, and diffusion coefficient, and from the interfacial property of surface tension. The term "thermophysical properties" includes all of the thermodynamic, transport, and interfacial properties.

NIST has had a long-standing program in fluid properties research, carried out at its Gaithersburg, Maryland, and Boulder, Colorado, laboratories, as well as at the original site of the National Bureau of Standards (NBS) in Washington, D.C. NIST's association with the refrigeration industry traces back to at least 1909 when ASHRAE (then ASRE) asked NBS to determine the properties of calcium chloride brines. In 1913 ASRE lobbied Congress to appropriate funds to NBS for research on ammonia. The project continued under ASRE sponsorship when federal funding ended. The tables resulting from this work (Bureau of Standards 1923) represented the accepted properties for this important fluid until they were superseded by a later NBS formulation (Haar and Gallagher 1978). Other early work of interest to the refrigeration industry included determination of the specific and latent heats of ice and the properties of steam. Some of the early data for ammonia and steam, notably the heat capacity and heat of vaporization data, are, to this day, considered to be among the very best—a remarkable achievement considering the primitive state of instrumentation at the time. Thus, NIST has been involved with refrigerants for 92 of its 100 years of existence. The work on refrigerants represents some of the first examples of NIST determining "standard values of constants"—accurate and authenticated determinations of the relations among physical quantities.

The Boulder program had its genesis in the 1950s as part of the former Cryogenics Division. Much of the early work was addressed to the needs of the space program and included

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hydrogen, oxygen, and other fuels and oxidizers. It later focused on the simple hydrocarbons and their mixtures and other fluids of industrial interest. Comprehensive measurement and modeling studies were carried out on these fluids; some of the resulting formulations are still the ones accepted as standards today.

The Boulder and Gaithersburg programs were merged into the Thermophysics Division in 1985. In a further reorganization in 1995, the division encompassed additional research areas to become the Physical and Chemical Properties Division. The National Bureau of Standards (NBS) became the National Institute of Standards and Technology (NIST) in 1988.

In 1981, when David Didion of the NIST Thermal Machinery Group initiated the program to investigate refrigerant mixtures as a means of increasing the efficiency of heat pumps, he recognized the need for property data and initiated a collaboration with Graham Morrison of the Physical and Chemical Properties Division. This was the genesis of the current program, which is the focus of this paper. The work in the Thermal Machinery Group includes machinery tests, cycle analysis, and heat-transfer research; these are described in a companion paper (Didion 2001).

## THE CSD EQUATION OF STATE

In 1981, only sparse data were available for the refrigerant mixtures being investigated in the heat pump work, and even some of the pure components were poorly characterized. Faced with this data situation, Morrison selected a simple equation of state<sup>1</sup> with a solid theoretical foundation—the Carnahan-Starling-DeSantis (CSD) equation—which expresses pressure as a function of temperature and molar volume:

$$\frac{PV}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y^3)} - \frac{a}{RT(V + b)}, \quad (1)$$

where

$$y = b/4V. \quad (2)$$

The first term is a theoretical expression for the repulsive forces resulting from the collisions of hard spheres. The second term is empirical and accounts for the attractive forces between molecules. The parameters  $a$  and  $b$  are simple, empirical functions of temperature. This model represents properties with a minimum of data and is easily extended to mixtures. A suite of Fortran subroutines implementing the CSD equation of state was developed by 1984. These were used in the NARM<sup>2</sup> research for the analysis of heat pump and heat-transfer test data and in cycle simulation models.

<sup>1</sup>. An equation of state is a mathematical formulation of the thermodynamic properties of a fluid. An equation of state allows, through integration and/or differentiation, the calculation of all of the thermodynamic properties, including those (such as entropy) that cannot be directly measured.

Sufficient data were available for most, but not all, of the pure refrigerants considered for the NARM work, but very limited data were available for the blends under consideration. Thus, experimental measurements of fluid properties were a component of the program from the very beginning. The early experimental work used primarily a “variable volume VLE (vapor-liquid equilibria) cell” to measure saturation properties of the blends and some of the pure fluids being studied in the cycle and heat-transfer research. The resulting data for vapor pressure and saturated liquid and vapor densities over a range of temperature were nearly optimal for fitting the CSD equation of state. By 1986, the CSD equation had been fitted to 11 pure refrigerants (based mostly on literature data) and 7 refrigerant blends (based on data measured at NIST).

By the mid-1980s, other groups were becoming interested in refrigerant blends and, of course, also recognized the need for refrigerant properties. They requested help from NIST, and between 1985 and 1989, we sent our Fortran subroutines to more than three dozen researchers in industry, academia, and other government laboratories. In those pre-Internet days, this meant mailing a magnetic tape or, later, a PC diskette. This phase was summarized in the NBS Technical Note of Morrison and McLinden (1986)—a report that eventually required three printings.

## ALTERNATIVE REFRIGERANTS

By early 1987, the evidence was mounting that the chlorofluorocarbon (CFC) refrigerants were destroying stratospheric ozone, which protects Earth from damaging ultraviolet radiation. We realized that NIST was in the unique position of actively researching the effect of “alternative” refrigerants on the performance of refrigeration equipment and at the same time having the in-house expertise to investigate both the properties and performance of new refrigerants. At that time, our “alternative” refrigerants were mixtures, most containing CFCs, but nonetheless the mental leap to shift focus to the environmentally acceptable fluids was small compared to many others in the industry.

Didion and McLinden determined that a systematic way of examining alternative refrigerants was needed and were asked to present their findings at the 1987 ASHRAE summer

<sup>2</sup>. Refrigerant blends have been variously referred to as nonazeotropic refrigerant mixtures (NARMs), zeotropic refrigerant mixtures, and nonazeotropic refrigerant blends (NARBs). The “nonazeotropic” designation was used in the early work to distinguish these blends from the azeotropes, such as R-502, which were the only blends in common use at the time. But “non” and “a” are both negative prefixes, leading to the current preference for simply “zeotropic mixture.” We at NIST have usually preferred the term “mixture” over “blend.” The current ASHRAE nomenclature standard uses “blend,” although earlier versions used “mixture.” The change came with the 1992 version, when some of the members of the standards project committee pointed out that in the chemical industry the term “blend” denoted an intentional mixing of components to achieve an improved product.

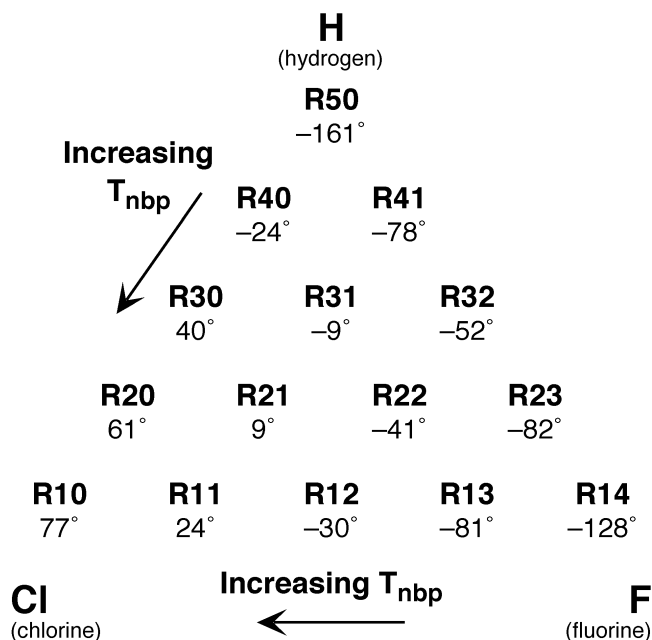


**Figure 1** Patterns in the normal boiling point temperature among the methane-based (one-carbon) halocarbon refrigerants (adapted from McLinden and Didion 1987).

meeting in Nashville. They started by examining the characteristics desirable of a refrigerant and stated that trade-offs between desirable properties were inevitable. The seemingly limitless choices were quickly whittled down. An examination of the work of Thomas Midgely, leading to the commercial introduction of the CFC refrigerants in the 1920s, revealed only a few elements that would form suitable compounds. A search of a database of 860 industrial fluids revealed only a small fraction with suitable thermodynamic characteristics, which also validated Midgely's list of elements. A theoretical analysis of optimum thermodynamic characteristics carried out at NIST indicated that small molecules were best suited to the vapor compression cycle. These three independent paths pointed to halocarbon compounds based on one or two carbon atoms. Recognizing that properties stemmed from molecular structure and varied in systematic ways, families of halocarbons were organized using triangular diagrams having the base hydrocarbon (methane or ethane) at the top; each lower row substituted one of the hydrogens with an atom of either fluorine or chlorine, with the fully halogenated CFCs at the bottom. These triangular diagrams revealed patterns in the boiling-point temperature (a key thermodynamic index), flammability, toxicity, and atmospheric lifetime (important in both ozone-depletion potential and greenhouse-warming potential). Figure 1 is the diagram for the boiling points of the methane-based compounds. Figure 2 is the summary diagram showing the trade-offs among desirable characteristics.

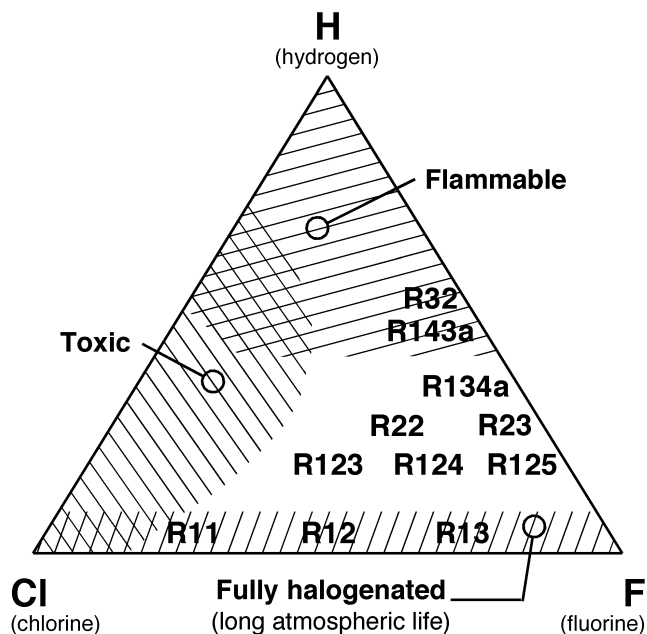


**Figure 2** Summary of the trade-offs among refrigerant characteristics (adapted from McLinden and Didion 1987); most of the “new” refrigerants are clustered in the region that is neither toxic nor flammable nor fully halogenated.

During the summer of 1987, negotiations leading to the Montreal Protocol were underway, and the presentation was received with great interest. It backed up the choice of R-123 and R-134a as the leading candidates to replace R-11 and R-12, respectively, with solid reasoning.<sup>3</sup> More importantly, it gave the refrigeration industry confidence that these were good choices, and that there was not some undiscovered “miracle fluid” that would soon make them obsolete. A paper for *ASHRAE Journal* (McLinden and Didion 1987) was based on the presentation. The manuscript was completed on September 16, 1987—the date of the signing of the Montreal Protocol. Timing is everything!

The first major project of the alternative refrigerants program was to measure and correlate the properties of R-134a and R-123. The introduction to the resulting paper described the situation: “Development efforts by equipment manufacturers have been hampered by property data that are sparse, conflicting, proprietary or, in some cases, simply unavailable” (McLinden et al. 1989a). This work presaged the entire program in a number of ways—it represented a comprehensive approach involving measurement, modeling, and delivery of the data in the form of tables, diagrams,

<sup>3</sup> Preliminary development of R-134a as a R-12 replacement was carried out by the chemical manufacturers in the 1970s in response to the original theory that CFCs depleted ozone. Further development was put aside in the intervening years because the magnitude of the potential depletion was thought to be small.

and a computer database. The support of NIST, the Department of Energy, the Environmental Protection Agency, and ASHRAE, as well as the donation of fluid samples from two major chemical suppliers, reflected the many parties interested in the work. The 12 authors listed on the paper hint at the great breadth of experience available at NIST and the close cooperation between them needed to bring such a project to fruition in a timely manner.

Any thought that replacing R-11 and R-12 with R-123 and R-134a would be the end of new refrigerants was quickly put to rest. The original 1987 Montreal Protocol had called for only a 50% reduction in CFC production and imposed no restrictions on HCFCs. Some thought that much of the remaining CFC production would be reserved for refrigeration uses. Early on, many in the industry hesitated even to discuss the need to eventually replace R-22, but we recognized the need to study R-22 alternatives, both as a contingency to avoid a repeat of the near-panic regarding the CFC phase-out should R-22 restrictions come to pass, and as part of the ongoing efforts in the Thermal Machinery Group to identify the fluids of highest efficiency. Subsequent revisions to the Montreal Protocol would, of course, mandate a complete phase-out of the CFCs and HCFCs, including R-22.

What was once a modest, though very fruitful, collaboration between Morrison and the Thermal Machinery Group quickly grew into a largely independent program involving a significant portion of the personnel and resources of the NIST Physical and Chemical Properties Division. The program would include experimental measurements, modeling, database development, and international activities. It would expand to include a wide variety of fluids and fluid mixtures. The early work focused on the thermodynamic properties but quickly expanded to include the transport properties. It was initially centered in the Gaithersburg part of the division, but it gradually shifted to the groups in Boulder. The two parts of the division had different capabilities, and the geographic shift occurred in response to evolving data needs (for example, the need for heat-capacity and transport-property data as fluids approached commercialization and the increasing importance of mixtures) and also to the retirement of several key Gaithersburg staff, as well as the premature death of Graham Morrison in 1993.

## Experimental Property Measurements

The measurement of fluid properties has been at the core of the NIST program on refrigerants. The experimental capabilities at NIST are easily the most comprehensive and wide-ranging anywhere in the world, considering both the variety of properties measured and the ranges of temperature and pressure covered. These capabilities had been built up over many years for projects on a wide variety of fluids and were rapidly applied to refrigerants research. Thus, NIST was able to provide crucial data in a timely fashion without the need to design and construct an entire array of apparatus.

The scope of the work may be appreciated by the work carried out just on R-134a, as summarized in Table 1. The work proceeded in several rounds. Preliminary measurements provided the minimal data needed to fit a first equation of state. This was soon followed by preliminary measurements and correlations of the transport properties (thermal conductivity and viscosity). As it became obvious that R-134a would see widespread commercial use, additional measurements were carried out to expand and improve the formulations. By 1994, the thermodynamic properties of R-134a were characterized well enough to consider R-134a as a “standard reference fluid.” Further research built on this, using R-134a to validate new experimental apparatus or develop new property models.

Among the NIST capabilities, several are noteworthy. The most essential data for a fluid are pressure-density-temperature ( $P$ - $\rho$ - $T$ ) data, and NIST has at least six different instruments operating on four distinct principles, again covering a wide range of temperature and pressure. In fitting equations of state we rely heavily on thermal data, including speed of sound and heat capacity at constant volume. Speed of sound is measured in several “resonators,” which have uncertainties of 0.01% or less; these data yield the heat capacity of the ideal gas as well as providing a check on the vapor-phase  $P$ - $\rho$ - $T$  data. NIST has two isochoric (constant-volume) calorimeters covering a combined temperature range of  $-243^{\circ}\text{C}$  to  $227^{\circ}\text{C}$  ( $-406^{\circ}\text{F}$  to  $440^{\circ}\text{F}$ ); they are the only calorimeters in the world routinely measuring  $C_v$  data. While isobaric ( $C_p$ ) heat capacities are more common, we find  $C_v$  data more useful in fitting equations of state. With roots in the former Cryogenics Division, we have many instruments that operate down to liquid nitrogen temperatures ( $-196^{\circ}\text{C}$  or  $-321^{\circ}\text{F}$ ) or lower, and while most refrigeration applications do not extend to such low temperatures, below-ambient capabilities are certainly necessary to fully characterize a refrigerant. (After all, a refrigerant, almost by its definition, operates in a cycle extending above, and below, ambient temperature.)

NIST has comprehensive capabilities for the measurement of viscosity and thermal conductivity. These transport properties are important for any working fluid. While the thermodynamic properties determine the theoretical efficiency in a given cycle, the transport properties have a large effect on heat-exchanger performance and, thus, on the economically feasible cycle efficiency. The main instruments applied to the refrigerants have been vibrating-crystal viscometers and transient hot-wire apparatus. For each property, we have one instrument operating from liquid nitrogen temperatures to slightly above ambient temperature and another covering the ambient to high temperature range. These have been supplemented by new or modified apparatus as described below.

Several instruments were developed specifically for the refrigerants. Vapor pressure is one of the most important thermodynamic properties and is especially important for a refrigerant. The standard, static technique for measuring vapor

**TABLE 1**  
**Measurements and Modeling Carried Out at NIST on R-134a**

| Range of Data or Model                             |                                 |               |                             |
|----------------------------------------------------|---------------------------------|---------------|-----------------------------|
| Type                                               | T (°C)                          | P (MPa)       | Reference                   |
| <b>Thermodynamic Property Measurements</b>         |                                 |               |                             |
| P- $\rho$ -T (vapor); vapor pressure               | 40 ~ 150                        | 0.2 ~ 5.3     | Weber (1989)                |
| Speed of sound and $C_p^\circ$ (vapor)             | -42 ~ 67                        | 0.10 ~ 3.0    | Goodwin & Moldover (1990)   |
| Surface tension                                    | -10 ~ 96                        | (sat'n)       | Chae et al. (1990)          |
| Dielectric constant and dipole moment              | 32 ~ 142                        | 0.02 ~ 0.8    | Meyer & Morrison (1991)     |
| VLE and P- $\rho$ -T (liquid)                      | -5 ~ 101                        | 0.7 ~ 5.8     | Morrison & Ward (1992)      |
| Vapor pressure                                     | -59 ~ -8                        | 0.02 ~ 0.2    | Goodwin et al. (1992)       |
| $C_v$ and P- $\rho$ -T (liquid)                    | -86 ~ 70                        | 2.6 ~ 35      | Magee (1992)                |
| Vapor pressure                                     | -93 ~ 77                        | 0.001 ~ 2.5   | Magee & Howley (1992)       |
| Saturation density                                 | 39~97                           | (sat'n)       | Niesen et al. (1994)        |
| P- $\rho$ -T (liquid and supercritical)            | -100 ~ 127                      | 1.7 ~ 35.     | Magee (1996)                |
| P- $\rho$ -T (liquid)                              | -30 ~ 98                        | 0.8 ~ 6.5     | Defibaugh & Moldover (1997) |
| <b>Determination of Critical Parameters</b>        |                                 |               |                             |
| Critical temperature                               | 101.055                         | -             | Chae et al. (1990)          |
| Critical T, P, $\rho$                              | 101.029                         | 4.068         | Morrison & Ward (1992)      |
| Critical density                                   | $\rho_c = 513.0 \text{ kg/m}^3$ |               | Van Poolen et al. (1994)    |
| <b>Transport Property Measurements</b>             |                                 |               |                             |
| Thermal conductivity                               | -73 ~ 117                       | 0.1 ~ 70.     | Laesecke et al. (1992)      |
| Viscosity (liquid)                                 | -103 ~ 47                       | 0.01 ~ 30.    | Diller et al. (1993)        |
| Viscosity (saturated liquid)                       | -23 ~ 33                        | (sat'n)       | Ripple & Matar (1993)       |
| Viscosity (saturated liquid)                       | -32 ~ 77                        | (sat'n)       | Laesecke et al. (1999)      |
| Thermal conductivity                               | -73 ~ 177                       | 0.1 ~ 70.     | Perkins et al. (2000)       |
| <b>Methods for the Analysis of Chemical Purity</b> |                                 |               |                             |
| Spectroscopic methods                              | -                               | -             | Bruno (1992a)               |
| Separation methods                                 | -                               | -             | Bruno (1992b)               |
| <b>Modeling</b>                                    |                                 |               |                             |
| MBWR EOS                                           | -40 ~ 177                       | 0 ~ 10.       | McLinden et al. (1989a)     |
| MBWR EOS                                           | -103 ~ 327                      | 0 ~ 70.       | Huber & McLinden (1992)     |
| Viscosity model                                    | -98 ~ 151                       | 0.1 ~ 34.     | Huber & Ely (1992a)         |
| Schmidt-Wagner EOS                                 | -103 ~ 177                      | 0 ~ 70.       | Huber & Ely (1992b)         |
| Thermal conductivity model                         | -73 ~ 117                       | 0.1 ~ 70.     | Huber et al. (1992)         |
| Vapor pressure model                               | -59 ~ 101                       | 0.02 ~ 4.1    | Huber (1994)                |
| Vapor pressure (from $C_{sat}$ )                   | -103 ~ -23                      | 0.0004 ~ 0.12 | Duarte-Garza & Magee (1997) |

pressure is subject to increasing errors and impurity effects at low pressures. To provide vapor pressure data of the highest accuracy, NIST built three separate “ebuliometers” (Weber and Silva 1994) in which the test fluid is continually boiled and condensed, sweeping impurities such as air out of the system. Measurements of vapor-liquid equilibria are among the most important for mixtures, and the existing NIST capabilities were augmented by a new VLE apparatus (Holcomb and Outcalt 1997) that simultaneously measures the density and composition of the liquid and vapor phases in equilibrium, along with the temperature and pressure; it also separately measures surface tension.

The standard method for measuring thermal conductivity employs an electrically heated wire in direct contact with the test fluid, and it is thus affected by the high polarity and very slight electrical conductivity of some of the new refrigerants. Two variations on this “transient hot wire” technique were developed: in the first, a bias voltage is applied to the heated wire to pre-charge the fluid surrounding it (Perkins et al. 1992), and in the second, a tantalum hot wire 25  $\mu\text{m}$  in diameter is insulated by a layer of tantalum pentoxide 0.07  $\mu\text{m}$  thick, created in situ by anodization (Perkins 1994). Some viscosity measurement techniques are also influenced by polarity, although to a lesser extent. The sealed capillary viscometer (Ripple and Defibaugh 1997), while limited to measurements on liquids at saturation, avoids such effects. All these new instruments operate over a wide range of temperatures, including below-ambient temperatures.

Many fluids have been investigated, and some of this work is outlined in Table 2. The fluids studied include all of the now-familiar “new” refrigerants—several that seemed promising, enjoyed a brief flurry of interest, but have returned to obscurity, and several of interest for niche applications. The efforts ranged from “primary data”—limited measurements (typically vapor pressure, saturated liquid density, and critical point) needed to fit generalized models such as the CSD equation of state or the extended corresponding states model (described below)—to the “comprehensive measurements” of multiple properties covering wide ranges of temperature and pressure needed to fit the many parameters in high-accuracy equations of state. Primary measurements were carried out on poorly characterized, but promising, fluids to provide the minimum data needed to evaluate their performance. Comprehensive measurements were reserved for fluids nearing commercial use. Between these extremes, limited “validation” measurements filled in gaps in the data or provided confirming data for otherwise well-characterized fluids.

The mixtures studied at NIST have ranged from the R-13B1/152a and R-22/114 blends of interest in the early heat pump work, to extensive measurements of the now

**TABLE 2**  
**Fluids Measured at NIST**

| Primary Data              |         |         |         |         |         |
|---------------------------|---------|---------|---------|---------|---------|
| R-123a                    | R-134   | R-142b  | R-143   | R-152   | R-227ea |
| R-236ea                   | R-245ca | R-245cb | R-245ea | R-245fa | R-218   |
| R-338mccq                 | R-13B1  | R-E125  | R-E134  | R-E245  | R-E263  |
| “Validation” Measurements |         |         |         |         |         |
| R-11                      | R-12    | R-13    | R-22    | R-23    | R-290   |
| R-600                     | R-600a  |         |         |         |         |
| Comprehensive Data        |         |         |         |         |         |
| R-123                     | R-124   | R-125   | R-134a  | R-141b  | R-143a  |
| R-152a                    | R-236fa | R-41    |         |         |         |

commercially available blends R-410A (R-32/125 [50/50]) and R-407C (R-32/125/134a [32/25/52]). A recent survey (McLinden et al. 1998b) of the mixture data available for blends of the HFCs R-32, R-125, R-143a, and R-134a, revealed that more than one-quarter of all published data sets were from NIST. More than 80% of the total number of heat capacity data points (including both  $C_v$  and  $C_p$ ) on refrigerant mixtures have been measured at NIST.

### Properties Modeling

The project on R-123 and R-134a (and many others to follow) specified that the experimental results be correlated with an equation of state. The CSD equation provided a usable representation of the data but not to the level we had obtained with the CFC refrigerants. The new refrigerants, especially the HFCs such as R-134a, were much more polar than the CFCs, and this presented difficulties in fitting the CSD equation of state. The solution was to employ a modified Benedict-Webb-Rubin (MBWR) equation of state for R-123 and R-134a. The MBWR equation was considerably more complex than the CSD equation, and this allowed the new data to be fitted accurately. The MBWR was not necessarily optimal for the refrigerants (it had been originally developed for nitrogen), but the computer programs necessary to fit it to data were available—providing another example of adapting existing NIST capabilities to accomplish the “need it yesterday” nature of many of the refrigerant tasks.

The MBWR equation expresses pressure as an explicit function of temperature and molar density and is of the form

$$P = \sum_{i=1}^9 a_i \rho^i + \exp(-\rho^2/\rho_{crit}^2) \sum_{i=10}^{15} a_i \rho^{2i-17}, \quad (3)$$

where the  $a_i$  are functions of temperature resulting in a total of

32 adjustable parameters. For a complete description of the energy quantities (enthalpy, entropy, etc.), the MBWR equation is combined with an expression for the molar heat capacity of the ideal-gas state, that is, vapor in the limit of zero pressure. The MBWR equation is thoroughly described by Younglove and McLinden (1994).

Many recent high-accuracy equations of state (e.g., Lemmon and Jacobsen 2001) have been expressed in terms of reduced molar Helmholtz energy using the general form:

$$\alpha = \frac{A}{RT} = \alpha^{id} + \sum_j N_j \tau^{t_j} \delta^{d_j} + \sum_k N_k \tau^{t_k} \delta^{d_k} \exp(-\delta^{l_k}), \quad (4)$$

where  $\alpha^{id}$  is the ideal-gas contribution, which is a function of the heat capacity of the ideal gas state. The summations in Equation 4 make up the residual, or real-fluid, contribution  $\alpha^r$ . The temperature and density are expressed in the dimensionless variables  $\tau = T^*/T$  and  $\delta = \rho/\rho^*$ , where  $T^*$  and  $\rho^*$  are reducing parameters, which are often the critical parameters. The  $N_j$  and  $N_k$  are numerical coefficients fitted to experimental data, and the exponents  $t_j$ ,  $t_k$ ,  $d_j$ ,  $d_k$ , and  $l_k$  are typically determined by a selection algorithm starting with a large bank of terms. The NIST equation of state work has gradually shifted to the Helmholtz-energy form, supplanting the MBWR equation by 1997.

The extended corresponding states (ECS) model has been adapted to the refrigerants (Huber and Ely 1994). It is especially useful for fluids with limited experimental data. The corresponding states concept is based on the assumption that, in reduced coordinates, different fluids obey the same intermolecular force laws. (A property is “reduced” by dividing by the corresponding critical point value.) This implies that, with the appropriate scaling of temperature and density, the reduced residual Helmholtz energies and compressibilities of an unknown fluid and of a reference fluid (for which an accurate, wide-ranging equation of state is available) are equal. Only limited data (typically vapor pressures and saturated liquid densities) are necessary to fit the “shape factors,” which scale the properties of a fluid onto those of the reference fluid. When combined with an expression for the ideal gas heat capacity, all other thermodynamic properties can be calculated.

The models used for mixtures parallel the pure-fluid equations. The early work used the CSD equation of state as described above. As focus shifted to the alternative refrigerants, the ECS method was used. More recently, we have adopted a new model developed in collaboration with the University of Idaho (Lemmon and Jacobsen 1999). This model applies mixing rules to the Helmholtz energy of the mixture components. It is a corresponding states method in the sense that the pure fluids are evaluated at conditions related to the reduced temperature and pressure of the mixture. But it allows the use of high-accuracy equations of state for the components, and the properties of the mixture will reduce

exactly to those of the pure components as the composition approaches a mole fraction of 1. The data required for a given mixture have also increased. The CSD and ECS models require only a few points at saturation to fit the one or two mixture parameters in those models. The mixture Helmholtz energy model requires extensive data to fit its mixing function; this function can be generalized using data on well-defined reference mixtures, however, so that additional blends require limited data.

The available data for the transport properties of viscosity and thermal conductivity are often limited, and this has necessitated a heavy reliance on generalized methods such as the ECS model. The ECS method that had been previously developed for the hydrocarbons was adapted for the refrigerants (Huber and Ely 1992a, Huber et al. 1992); the major modification was the use of R-134a as the reference fluid. The ECS method was further extended by the addition of a “viscosity shape factor” and a “thermal-conductivity shape factor” (Klein et al. 1997; McLinden et al. 2000). These additional shape factors were fitted to experimental data; they bridged the gap between the traditional ECS method—which required very little data but likewise did not make use of data away from saturation—and a full-blown fluid-specific correlation of extensive data.

With this variety of models, we are able to represent fluids with very limited data as well as to provide high-accuracy formulations for the refrigerants with extensive data. The presence of both experimental and modeling groups at NIST has provided considerable synergy. As an example, during the development of a revised MBWR equation of state for R-123 (Younglove and McLinden 1994), we concluded that additional heat capacity data were needed to accurately describe the compressed liquid region. Facing a looming deadline for submitting an equation of state to the IEA Annex 18 evaluations (described below), we were able to carry out the needed measurements of  $C_p$  and incorporate them into the equation of state only hours after they were measured.

## The Natural Refrigerants

Interest in the use of naturally occurring fluids as refrigerants has increased tremendously in recent years. But these fluids are not new to NIST. As mentioned above, NIST first started work on ammonia in 1913. In the 1980s, NIST had a major program to measure and correlate the properties of industrial fluids including carbon dioxide, ammonia, propane, and isobutane. The motivation for this work came primarily from the natural gas industry, not from refrigeration. But many of the experimental apparatus and modeling tools developed in this work were later applied to the refrigerants. With the resurgence of interest in the natural refrigerants in the 1990s, it was a simple matter to recognize that, for example, R-290 and R-744 were just alternative names for propane and carbon dioxide and make the data available to the refrigeration industry.

## The NIST REFPROP Database

The Fortran subroutines implementing the CSD equation of state were in increasing demand by 1988, and the decision was made to release them as a formal NIST product called a “Standard Reference Database.” Version 1.0 of the *NIST Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database* (better known by the acronym REFPROP, for REfrigerant PROPERTIES) was released in 1989 (McLinden et al. 1989a) and distributed by the Standard Reference Data Program of NIST. The program combined the Fortran subroutines with a simple text-based user interface. The initial version contained CSD equations of state for the 11 refrigerants from the 1986 Technical Note, plus R-123, R-124, R-134, and R-134a. The program could calculate properties of only binary (two-component) blends. Mixture parameters for 20 blends were included.

Regular updates to NIST REFPROP followed, incorporating additional fluids, additional properties (for example, viscosity and thermal conductivity were added with version 3.0 [Gallagher et al. 1991]), additional property models, and other capabilities. These are highlighted in Table 3. The REFPROP database was increasingly used as the “end product” for the NIST work on refrigerant properties, and a number of projects funded by outside agencies specified inclusion of the results in REFPROP as a contract deliverable.

By Version 5, the database was showing its age, and the general design of a completely revised REFPROP code was laid out. The core property routines would be modular to facilitate the addition of new fluids and new models. It would also feature a modern, Windows-based user interface. The result was version 6 of REFPROP (McLinden et al. 1998a). A major objective in version 6 was to implement the most accurate models available. High-accuracy equations of state, either a Helmholtz-energy formulation or an MBWR equation, were used where available. The ECS model was used for fluids with more limited data.

Missing from version 6 was the CSD equation of state. The move from the CSD equation to the MBWR and Helmholtz-energy models paralleled the development of the fluids themselves. Between 1981 and the present, R-134a, for example, went from being an obscure fluid familiar only to specialist chemists to the dominant refrigerant in many applications. The CSD equation was an excellent choice in 1981 when the data for many of the fluids were very limited, but other models could provide more accurate results where sufficient data were available. We had long recognized that the CSD equation did not accurately represent the critical region. This was a moot point for fluids such as R-12 that operate well below the critical temperature, but the increasing importance of fluids with lower critical temperatures, such as R-32, R-125, R-143a, and their blends, proved to be the final Achilles’ heel for the CSD equation of state.

## International Activities and Conferences

In view of the existence of multiple approaches to the important problem of representing the properties of the new refrigerants and their mixtures, it was desirable to select standard formulations for use by the refrigeration industry. In 1990, NIST organized a group under the auspices of the Heat Pump Programme of the International Energy Agency to address this issue. Eight member countries (Austria, Canada, Germany, Japan, Norway, Sweden, the United Kingdom, and the United States) joined together to form Annex 18—Thermophysical Properties of the Environmentally Acceptable Refrigerants. One of the goals of this Annex (or programme working group) was to evaluate the available models and recommend formulations as international standards. Annex 18 evaluated equations of state for R-123, R-134a, R-32, R-125, and R-143a and recommended formulations as international standards. It also examined available mixture models. The Annex presented its final report at the 1999 IIR Congress in Sydney (McLinden and Watanabe 1999).

**TABLE 3**  
**Summary of the NIST REFPROP Database**

| Version | Release date | Fluids                      | Mixtures | Key new features                                                                                                                                                                         |
|---------|--------------|-----------------------------|----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1.0     | 12/1989      | 15                          | 20       | CSD EOS, pure fluids, and binary mixtures                                                                                                                                                |
| 2.0     | 3/1991       | 18                          | 24       | 5-component mixtures allowed                                                                                                                                                             |
| 3.0     | 12/1991      | 26 (including R-290)        | 37       | Predictive scheme for mixtures without data; transport; properties using ECS model; ECS model as option for thermo properties                                                            |
| 4.0     | 11/1993      | 38 (including R-717, R-744) | 60       | MBWR EOS for 11 pure fluids as option; ECS model is recommended option for other fluids                                                                                                  |
| 5.0     | 2/1996       | 43                          | 60       | MBWR EOS for 3 additional fluids; ECS model as option for mixtures                                                                                                                       |
| 6.0     | 7/1998       | 33                          | 79       | Complete revision of Fortran code<br>Graphical user interface<br>Implements most-accurate models available: MBWR, Helmholtz, and/or ECS EOS; standard mixtures (e.g., R-410A) predefined |

NIST staff also participated in committees and working groups convened by the United Nations Environmental Programme, the International Union of Pure and Applied Chemistry, and the industry-sponsored Alternative Fluorocarbon Environmental Acceptability Study and Alternative Refrigerant Evaluation Program.

Numerous conferences and workshops have been devoted to the alternative refrigerants, especially from 1987 to about 1993. NIST participated in many of these and hosted several. In 1988, NIST gathered industry experts together to help define the property data needs for the new refrigerants. The Building Environment Division hosted three major conferences in Gaithersburg (co-sponsored by ASHRAE) on the alternative refrigerants as described by Didion (2001). Also significant are the triennial Symposia on Thermophysical Properties, organized largely by the Physical and Chemical Properties Division, and held in Gaithersburg or Boulder. Beginning with the 10th Symposium in 1988, these became a prime venue for fluid-property specialists from around the world to present their findings on refrigerants. The 13th Symposium in 1997 featured 65 presentations in 13 special sessions devoted to properties of refrigerants.

### Chemical Kinetics of Refrigerants

NIST has also extensively studied the chemical reaction kinetics of refrigerants in the atmosphere. While this topic is outside the scope of this paper and may perhaps lie outside the direct interest of most ASHRAE members, these data are essential for determining the atmospheric lifetime and potential environmental effects and, thus, acceptability of a refrigerant. This work has included authorship or co-authorship of more than 20 evaluated reviews of kinetic and photochemical data for use in global atmospheric modeling.

### CONCLUSIONS

NIST has made significant contributions to the refrigeration industry through its measurement, modeling, and database efforts on the properties of the "alternative" refrigerants. This comprehensive program was driven by the needs of the refrigeration industry. NIST was in a unique position to respond to this urgent national and international need because of its long-standing program in fluid properties.

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