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Development of the REFPROP Database and Transport Properties of Refrigerants

Final Report

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EXECUTIVE SUMMARY

Development of REFPROP

This task consisted of developing Version 6.0 of the NIST Thermodynamic and Transport Properties of Refrigerants and Refrigerant Mixtures Database (REFPROP), entailing a complete revision of this database. This program is based on the most accurate pure fluid and mixture models currently available. The database development is further divided into the development of a graphical user interface and the development of Fortran subroutines which implement the property models.

Three models are used for the thermodynamic properties of pure components, depending on the availability of data. The first is the modified Benedict-Webb-Rubin (MBWR) equation of state. It is capable of accurately representing the properties of a fluid over wide ranges of temperature, pressure, and density. The MBWR equation is the basis for the current international standard for the properties of R123 (Younglove and McLinden, 1994). The second high-accuracy pure-fluid equation of state is written in terms of reduced molar Helmholtz free energy. This "Helmholtz energy model" is the basis for the international standard formulation for R134a (Tillner-Roth and Baehr, 1994). The third pure-fluid model is the extended corresponding states (ECS) model of Huber and Ely (1994). It is used for fluids with limited experimental data.

The thermodynamic properties of mixtures are calculated with a new model which was developed, in slightly different forms, independently by Tillner-Roth (1993) and Lemmon (1996) (see also Lemmon and Jacobsen, 1997). It applies mixing rules to the Helmholtz energy of the mixture components. The Lemmon-Jacobsen model provides a number of advantages. By applying mixing rules to the Helmholtz energy of the mixture components, it allows the use of high-accuracy equations of state for the components, and the properties of the mixture will reduce exactly to the pure components as the composition approaches a mole fraction of 1. Different components in a mixture may be modeled with different forms; for example, a MBWR equation may be mixed with a Helmholtz equation of state. The mixture is modeled in a fundamental way, and thus the departure function is a relatively small contribution to the total Helmholtz energy for most refrigerant mixtures. The great flexibility of the adjustable parameters in this model allows an accurate representation of a wide variety of mixtures, provided sufficient experimental data are available.

The mixing parameters have been fitted to experimental data for 75 binary pairs. For mixtures lacking experimental data a predictive model, based on the fundamental molecular parameters dipole moment, acentric factor, and critical parameters, is used. This model is described in Appendix B. Mixture properties calculated with this model will have a larger uncertainty than those based on experimental data. Furthermore, the data used to develop this predictive model were for mixtures of HFCs, CFCs, HCFCs, hydrocarbons, and carbon dioxide. Its applicability to different types of mixtures, such as ammonia plus an HFC, is unknown.

The transport properties of pure fluids are modeled with either fluid-specific correlations taken from the literature or a new variation on the extended corresponding states model. This new model is described below and in Appendix C. Mixtures are modeled with the ECS approach.

The property models described above are implemented as a suite of FORTRAN subroutines. These routines have been completely rewritten from earlier versions of REFPROP. Source code is provided with the database so that users may link the property routines with their own application. The routines are written in ANSI-standard FORTRAN 77 and are compatible with FORTRAN 90. They are written in a structured format, are internally documented with extensive comments, and have been tested on a variety of compilers.

The fluid or mixture of interest is specified with a (required) call to the subroutine "SETUP." This routine reads the coefficients to the NIST-recommended models for that fluid. Alternative property models and/or nonstandard reference states may be specified by calls to additional (optional) setup routines. Routines are provided to calculate thermodynamic and transport properties and surface tension at a given (T, ρ, x) state. Iterative routines provide saturation properties at a specified (T, x) or (P, x) state. Flash calculations calculate single- or two-phase states at specified (P, h, x), (P, T, x), etc.

The routines mentioned above are independent of the model. Underlying these routines are sets of "core" routines for each of the models implemented in the database. Each such set is highly modular and is contained in a separate file. Coefficients needed for a particular model are stored in common blocks, but these commons are referenced only by routines in the same file. These sets of subroutines, thus, resemble "units" in the Pascal language with clearly demarcated "interface" and "local" declarations. This structure is intended to simplify the addition of future models to the database and will make such additions almost totally transparent to the user.

Numerical coefficients to the property models are stored in text files. There is one file per fluid and one file containing coefficients for the mixture departure functions. These files are read (once) upon the call to SETUP. NIST REFPROP contains 33 pure fluids and can calculate properties for mixtures with up to five components. Fluids in the database include environmentally acceptable HFCs, such as R23, R32, R125, R134a, and R245fa; HCFCs, such as R22, R123, R124, R141b, and R142b; traditional CFCs, such as R11, R12, R13, R113, R114, and R115; and "natural" refrigerants, such as ammonia, carbon dioxide, propane, and isobutane. The fluids included in the database are listed in Table 1. NIST will add fluids to the database as commercial interest and the availability of data allow, and we welcome suggestions for new fluids.

The user interface provides a convenient means to calculate and display thermodynamic and transport properties. It is written for the Windows™ operating system. The interface is written in Pascal; it accesses the FORTRAN property subroutines via a dynamic link library. The program is controlled through the use of the following pull-down menus:

> File provides commands to save and print generated tables and plots. Individual items or entire sessions with multiple windows may be saved or recalled. The standard "print setup" and "exit" commands are also present.
>
> The Edit menu provides copy and paste commands which allow selected data to be exchanged with other applications.
>
> The Options menu provides commands for selecting the unit system, properties of interest, and the reference state. These options may be stored for recall at a later time. A user-defined set of preferences is loaded upon program startup.
>
> The pure fluid or mixture of interest is specified with commands in the Substance menu. Most of the refrigerant mixtures of current commercial interest (those having an ASHRAE R400 or R500-series designation) are predefined. In addition, new mixtures can be specified and saved by combining up to five pure components.
>
> The Calculate menu initiates the calculations that generate a property table. Each property selected for display is shown in a separate column of the table. Two types of tables are provided. The first type provides properties at saturation or with a property (such as temperature or pressure) held constant with another selected property varying over a specified range. The second type allows the user to select the independent

variables. Values of the independent variables may then be entered with the keyboard, read from a file, or pasted from another application.

The Plot menu provides high-quality x-y plots of any variables appearing in a table. In addition, temperature-entropy, pressure-enthalpy, temperature-composition and pressure-composition diagrams may be generated automatically. Controls are provided to modify the plot size, axis scaling, plot symbols, line type, legend, and other plot features.

Each table or plot appears in a separate window and can be accessed, resized, or retitled with commands in the Window menu. The number of windows is limited only by available memory.

A complete online-help system can be accessed through the Help menu.

A status line at the bottom of the screen displays the currently specified mixture, composition, and reference state. Clicking on the status line will call up a screen for each of the components providing documentation for fluid constants, the source of the models, and their range of applicability.

The database calculates seventeen thermodynamic and transport properties, including surface tensions of pure fluids and mixtures. Commercialized blends, such as R407C and R410A, are predefined in the interface and are listed in Table 2.

Modeling of Transport Properties with Extended Corresponding States

We have developed a new model for the thermal conductivity of refrigerants based on the extended corresponding states (ECS) concept. The principle of corresponding states stems from the observation that the properties of many fluids are similar when scaled according by their respective critical temperature and density. Extended corresponding states models modify this scaling by additional "shape factors" to improve the representation of data. ECS methods have often been used to represent both the thermodynamic and transport properties of a fluid, especially fluids with limited data. Recently, high-accuracy equations of state have been developed for many of the refrigerants of industrial interest. But, the situation for the transport properties of viscosity and thermal conductivity lags the thermodynamic properties—accurate, wide-ranging, fluid-specific correlations are available for only a few refrigerants. There is a need for a method which can predict the transport properties in the absence of data yet also take advantage of whatever experimental data might be available to improve upon the purely predictive scheme.

The method we present starts with the ECS model of Huber et al. (1992). We combine this predictive model with the best available thermodynamic equations of state. Furthermore, when thermal conductivity data are available, we use those data to fit a new "thermal conductivity shape factor" and/or a term in the traditional correlation for the dilute-gas portion of the thermal conductivity. Use of these additional factors results in significantly improved agreement between the ECS predictions and experimental data. The method has been applied to 11 halocarbon refrigerants and ammonia. The average absolute deviations between the calculated and experimental thermal conductivity values are 4% or less for 10 of the 12 fluids studied. This new model is analogous to our parallel work on viscosity (Klein et al. 1997). It accomplishes more than what was set out in the original task statement in that all available data (not just data at saturation) can be used in fitting the shape factors.

Details of this model are presented in Appendix C. This Appendix forms the basis of a paper which will be submitted for publication in the *International Journal of Refrigeration.*

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Table 1. Fluids in the REFPROP Database

Short Name	CAS number	Full Chemical Name
ammonia	7664-41-7	ammonia
butane	106-97-8	butane
carbon dioxide	124-38-9	carbon dioxide
ethane	74-84-0	ethane
isobutane	75-28-5	2–methylpropane
propane	74-98-6	propane
propylene	115-07-1	propene
R11	75-69-4	trichlorofluoromethane
R12	75-71-8	dichlorodifluoromethane
R13	75-72-9	chlorotrifluoromethane
R14	75-73-0	tetrafluoromethane
R22	75-45-6	chlorodifluoromethane
R23	75-46-7	trifluoromethane
R32	75-10-5	difluoromethane
R41	593-53-3	fluoromethane
R113	76-13-1	1,1,2–trichloro–1,2,2–trifluoroethane
R114	76-14-2	1,2–dichloro–1,1,2,2–tetrafluoroethane
R115	76-15-3	chloropentafluoroethane
R116	76-16-4	hexafluoroethane
R123	306-83-2	1,1–dichloro–2,2,2–trifluoroethane
R124	2837-89-0	1–chloro–1,2,2,2–tetrafluoroethane
R125	354-33-6	pentafluoroethane
R134	359-35-3	1,1,2,2–tetrafluoroethane
R134a	811-97-2	1,1,1,2–tetrafluoroethane
R141b	1717-00-6	1,1–dichloro–1–fluoroethane
R142b	75-68-3	1–chloro–1,1–difluoroethane
R143a	420-46-2	1,1,1–trifluoroethane
R152a	75-37-6	1,1-difluoroethane
RC318	115-25-3	octafluorocyclobutane
R227ea	431-89-0	1,1,1,2,3,3,3–heptafluoropropane
R236ea	431-63-0	1,1,1,2,3,3–hexafluoropropane
R236fa	690-39-1	1,1,1,3,3,3–hexafluoropropane
R245ca	679-86-7	1,1,2,2,3–pentafluoropropane
R245fa	460-73-11	1,1,1,3,3–pentafluoropropane

Table 2. Predefined Mixtures in the REFPROP Database

ASHRAE Designation	Components	Composition (mass percentages)
R401A	R22/152a/124	53/13/34
R401B	R22/152a/124	61/11/28
R401C	R22/152a/124	33/15/52
R402A	R125/290/22	60/2/38
R402B	R125/290/22	38/2/60
R404A	R125/143a/134a	44/52/4
R405A	R22/152a/142b/C318	45/7/5.5/42.5
R406A	R22/600a/142b	55/4/41
R407A	R32/125/134a	20/40/40
R407B	R32/125/134a	10/70/20
R407C	R32/125/134a	23/25/52
R407D	R32/125/134a	15/15/70
R407E	R32/125/134a	25/15/60
R408A	R125/143a/22	7/46/47
R409A	R22/124/142b	60/25/15
R409B	R22/124/142b	65/25/10
R410A	R32/125	50/50
R410B	R32/125	45/55
R411A	R1270/22/152a	1.5/87.5/11.0
R411B	R1270/22/152a	3/94/3
R414B	R22/124/600a/142b	50/39/1.5/9.5
R500	R12/152a	73.8/26.2
R501	R22/12	75/25
R502	R22/115	48.8/51.2
R503	R23/13	40.1/59.9
R504	R32/115	48.2/51.8
R507A	R125/143a	50/50
R508A	R23/116	39/61
R508B	R23/116	46/54

APPENDIX A

Task Statement

Development of REFPROP

The REFPROP database program is widely used in the refrigeration industry for the calculation of refrigerant properties. This program had its origins as a tool for investigating refrigerant mixtures at a time when property data on mixtures (and even many pure fluids) were extremely limited. Given the data situation in the early 1980's, the program was based on the Carnahan-Starling-DeSantis (CSD) equation of state—a model which does a reasonable job of calculating near-saturation properties with limited input data. Over the years, we have added the extended corresponding states (ECS) model and modified Bennedict-Webb-Rubin (MBWR) equations of state for selected pure fluids. Even so, the database has not always kept up with the demands of industry—with the commercialization of refrigerant blends, accuracy demands for mixtures have increased; also, fluids such as R32 and R125 are used much closer to the critical point than traditional refrigerants. In addition, the user interface to REFPROP is not the most modern.

We propose both a major upgrade of the capabilities of REFPROP and a complete rewrite of the code. We would retain the MBWR and ECS models and add at least two new models for the thermodynamic properties: the so-called "fundamental" equation of state for pure fluids and a Helmholtz energy model for mixtures. The University of Idaho and at least two groups in Germany have produced high-quality fits of several fluids using the fundamental equation of state; including this model would allow us to use their equations for fluids, such as R22, for which we do not have MBWR equations.

The mixture Helmholtz model is under development at NIST (in cooperation with the University of Hannover, Germany) and at the University of Idaho (under contract to NIST). This model shares many concepts with the ECS model, but it applies mixing rules to the Helmholtz free energy of each of the mixture components rather than referencing properties to a single pure reference fluid as is the case with the ECS model. It thus starts with high-accuracy properties for each of the mixture components (mixture properties can be no better than the constituent pure components) and reduces exactly to the pure components at the limits of composition. It is simpler (and should thus be faster) than the ECS model. The mixture Helmholtz model was shown to be clearly superior to both ECS and cubic equations of state in a preliminary comparison of mixture models conducted by IEA Annex 18. Although further development work is needed to incorporate additional fluids and mixtures into this scheme, it is the most promising model currently available and should satisfy the accuracy demands of the refrigeration industry.

The ECS model is still the best comprehensive model available for the transport properties of mixtures and would be retained. We would also add high-accuracy transport correlations for selected pure fluids as available in the literature. A model for surface tension would be added.

We would also add a modern graphical user interface (GUI) which would allow easier access to options, multiple calculation windows, plotting capabilities, and easy cut-and-paste data transfer to spreadsheets. Of equal significance for users of the core subroutines, we would completely restructure and rewrite the code to make it modular, more understandable, and more robust. Fluid-specific coefficients would be stored in data files (rather than compiled Fortran block data routines) making it much easier to update fluids or add new fluids.

Modeling of pure-fluid transport properties

We use several different approaches to model pure-fluid transport properties. For fluids with extensive data, we develop fluid-specific surfaces for the viscosity and thermal conductivity as functions of temperature and density. For fluids with limited data, we use variations of the extended corresponding states (ECS) model. The ECS model uses a "transport shape factor" in addition to the two shape factors for the thermodynamic properties together with viscosity and thermal conductivity surfaces for a reference fluid (R134a in the case of refrigerants). This transport shape factor is based on saturated liquid viscosities, if available; in the absence of data, it is based on a generalized correlation involving the acentric factor.

Each of these approaches could be improved. Some of the more important pure fluids warrant fluid-specific surfaces. In particular, the surface for R134a, which serves as the reference surface in the ECS model is in need of an update—considerable new data have become available since the present surface was fitted in 1992. The ECS approach based on saturated liquid viscosities works well, but needs to be updated with recent experimental data and refit to the new R134a reference surface. This approach is somewhat limited in that it cannot make use of data away from saturation. For some fluids, single-phase data are available, which, while not sufficient for a fluid-specific surface, would be valuable in fitting a fluid. At present, we must discard these data because the current implementation of the ECS model is not able to make use of them. The generalized ECS approach needs further development; again, recently available data will allow an improvement of this approach.

As a first phase in this area, we propose to fit high-accuracy viscosity and thermal conductivity surfaces for R134a, for pure-fluid uses and as a reference fluid for the ECS model. We will compile all available data for the common HFC and HCFC refrigerants, and use these data to update the ECS model based on saturation data.

APPENDIX B

A Predictive Model for Refrigerant Mixures

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Version 6 of the REFPROP database implements a new model for the thermodynamic properties of mixtures. This model applies mixing rules to the Helmholtz free energy of each of the mixture components. It starts with high–accuracy properties for each of the mixture components (mixture properties can be no better than the constituent pure components) and reduces exactly to the pure components at the limits of composition. This mixture Helmholtz model makes use of a generalized mixing function which is applicable to entire classes of fluids. This generalized function is modified by a multiplier, F_{pq}, and reducing parameters k_T and k_V for particular mixtures. This approach allows a highly accurate representation of mixtures with extensive data. This Appendix describes a predictive scheme for the k_T parameter in the mixture Helmholtz model based on the fundamental molecular parameters dipole moment, acentric factor, and critical parameters. The k_T parameter is the most important of the three and has the closest parallels with the mixing parameters in other mixture models.

Mixture data for a total of 75 binary pairs have been collected for use in this modeling task. About three–fourths of the binary pairs contain an HCFC and/or CFC and, so, will not be applicable for use in refrigeration equipment. Nevertheless, the HCFC and CFC-containing mixtures have provided a wider range of molecular parameters which has proven useful for developing the predictive model. (For example, the HFCs are highly polar while the hydrocarbons are nonpolar; the CFCs and HCFCs provide intermediate values of dipole moment.) These data have been evaluated, and while their quality varies widely, they provide a sufficient database of VLE data.

The model takes the form of correlation for the ζ_{12} parameter. The ζ_{12} parameter is equivalent to the more familiar k_T parameter, with the conversion between them given by:

$$k_T = 1 + 2\frac{\zeta_{12}}{T_1^{crit} + T_2^{crit}} \tag{1}$$

A wide variety of fluid parameters were examined in developing the predictive method; these included the dipole moment, molecular volume, acentric factor, critical temperature, critical pressure, critical density, triple point temperature, and the normal boiling point temperature. Of these, only the critical temperature T^{crit}, critical pressure P^{crit}, and acentric factor ω were used in the final scheme to calculate ζ_{12}. The dipole moment μ was used to determine the order of the inputs to the scheme. ζ_{12} is given by

$$\zeta_{12} = \left(\frac{T_2^{crit}}{T_1^{crit}}\right)\left\{40.4 - 25.03\exp\left[0.69315\frac{T_1^{crit}P_2^{crit}\omega_2}{T_2^{crit}P_1^{crit}\omega_1}\right]\right\}, \tag{3}$$

where fluid "1" is the one with the smaller value of the dipole moment. In the special case where the dipole moments of the two fluids are identical, fluid "1" is the fluid with the larger value of:

$$\frac{T^{crit}}{P^{crit}\omega}. \tag{4}$$

The value of ζ_{12} ranges between –100 and +20. A value of zero for ζ_{12} corresponds to ideal mixing. In most cases, the predictive scheme predicts ζ_{12} within ± 20. Even for one of the worst cases, the propylene/R115 mixture, using the predicted ζ_{12} value of –18 instead of the experimental value of –41 increases the average absolute deviation in bubble–point pressure only from 1.5% to 4.5%. For most of the other systems, deviations using the predicted value will be much less. The values of ζ_{12} calculated from experimental data and those predicted by Equation 3 are given in Table B-1.

A method for predicting the other parameters, F_{pq} and k_V, is still unavailable due to lack of experimental data. The ζ_{12} parameter is the most important of the three and even this one parameter captures the most essential features of mixture behavior, including the azeotropic behavior that exists in some of the fluid pairs. With this parameter alone, vapor–liquid equilibria for nearly all systems can be calculated with acceptable uncertainty. The largest influence of the F_{pq} and ξ_{12} parameters is in the calculation of densities. When only the ζ_{12} parameter is used, densities are generally calculated within 1% of experimental measurements.

Of course, one of the major results of this task is the fitting of experimentally based values of ζ_{12}, and these should be used when available. But in the case of two mixtures, R23/134a and CO_2/R12, the experimental data were of questionable accuracy, and we feel that using the predicted value will give more reliable results for the mixture properties. Likewise, the new mixture prediction scheme does not replace the values of F_{pq}, ζ_{12}, and ξ_{12} determined in previous work for binary mixtures with extensive data, including mixtures of R32, R125, R134a, R152a, and R143a; mixtures of propane with R32, R125, and R134a; and the mixture CO_2/R41.

Table B-1. Values of ζ_{12} evaluated from experimental data and calculated from Equation 3.

Mixture	ζ_{12}—fit to experimental data	ζ_{12}—calculated with predictive model
Propane/R32	–102.34	–106.11
Propane/R22	–43.44	–41.14
Propane/R115	–41.19	–19.15
Propane/R125	–74.31	–45.99
Propane/R134a	–73.73	–62.26
Propylene/R12	–8.75	–12.91
Propylene/R13	–31.18	–16.13
Propylene/R22	–15.86	–39.14
Propylene/R23	–62.15	–72.84
Propylene/R114	–21.87	–14.85
Propylene/R115	–41.09	–18.06
Propylene/R116	–79.47	–23.10
Propylene/R134a	–46.98	–59.26
Propylene/R142b	–8.04	–26.17
Propylene/R152a	–37.88	–48.83
CO_2/R12†	–37.06	10.63
CO_2/R22	–0.62	4.59
CO_2/R23	–12.26	–2.64
CO_2/R32	–3.12	–5.02
CO_2/R41	1.79	0.04
CO_2/R142b	–15.84	8.51
R11/12	–0.53	–10.58
R11/13	–7.87	–13.11
R11/22	–26.89	–31.62
R11/23	–67.26	–58.90
R12/13	–13.44	–12.61
R12/22	–22.32	–31.44
R12/23	–55.24	–58.52
R12/32	–71.97	–80.66
R12/113	20.16	–8.48
R12/114	–2.04	–11.18
R12/134a	–45.30	–47.78
R12/142b	–22.24	–20.66
R12/143a	–34.22	–26.35
R12/152a	–44.30	–39.32
R13/14	–9.08	–2.99
R13/23	–40.35	–51.35
R13/113	12.71	–4.03
R14/23	–32.70	–36.63
R21/114	–34.61	–18.67
R22/23	–10.68	–21.80
R22/32	–5.05	–30.19
R22/113	–27.29	–30.89

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† The experimental data for this system are questionable, and the calculated value of ζ_{12} is recommended in preference to the experimental value.

Table B-1 (continued).

Mixture	ζ_{12}—fit to experimental data	ζ_{12}—calculated with predictive model
R22/114	–25.51	–27.71
R22/115	–40.47	–24.02
R22/124	–18.64	–6.24
R22/125	–16.52	–11.76
R22/134a	–6.89	–16.86
R22/142b	0.23	–3.93
R22/152a	6.36	–13.02
R23/113	–63.32	–57.56
R23/114	–57.97	–51.62
R23/116	–51.22	–37.04
R23/134a†	40.90	–5.22
R32/115	–83.98	–62.65
R32/125	–14.54	–26.74
R32/134a	–6.14	–2.69
R32/143a	–17.00	1.76
R32/152a	–2.64	–0.47
R113/114	0.24	–7.19
R113/142b	–17.64	–20.74
R113/152a	–52.63	–38.52
R114/115	–2.15	–6.76
R114/152a	–40.56	–34.68
R116/134a	–42.80	–29.59
R123/134a	–21.73	–27.74
R124/134a	–9.93	–21.84
R124/142b	–1.46	–7.12
R124/152a	–4.78	–17.43
R125/134a	–2.00	–14.30
R125/143a	3.06	–5.71
R134a/142b	–11.07	0.23
R134a/143a	1.52	–3.04
R134a/152a	0.87	–6.76
R142b/152a	–13.37	–21.15

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† The experimental data for this system are questionable, and the calculated value of ζ_{12} is recommended in preference to the experimental value.

APPENDIX C

An Extended Corresponding States Model for the Thermal Conductivity of Refrigerants[1]

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ABSTRACT

The extended corresponding states (ECS) model of Huber et al. (*Fluid Phase Equilibria*, 1992, **80**, 249–261) for calculating the thermal conductivity of a refrigerant is modified by the introduction of a thermal conductivity shape factor which is determined from experimental data. An additional empirical correction to the traditional Eucken correlation for the dilute-gas conductivity was found to be necessary, especially for highly polar fluids. Use of these additional factors results in significantly improved agreement between the ECS predictions and experimental data. The method has been applied to 11 halocarbon refrigerants and ammonia. The average absolute deviations between the calculated and experimental thermal conductivity values are 4% or less for 10 of the 12 fluids studied.

KEYWORDS

refrigerant; thermal conductivity; model; calculation; corresponding states

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INTRODUCTION

We present a new model for the thermal conductivity of refrigerants based on the extended corresponding states (ECS) concept. The principle of corresponding states stems from the observation that the properties of many fluids are similar when scaled according by their respective critical temperature and density. The extended corresponding states models modify this scaling by additional "shape factors" to improve the representation of data. ECS methods have often been used to represent both the thermodynamic and transport properties of a fluid, especially fluids with limited data. Recently, high-accuracy equations of state have been developed for many of the refrigerants of industrial interest. But, the situation for the transport properties of viscosity and thermal conductivity lags the thermodynamic properties—accurate, wide-ranging, fluid-specific correlations are available for only a few refrigerants. There is a need for a method which can predict the transport properties in the absence of data yet also take advantage of whatever experimental data might be available to improve upon the purely predictive scheme.

The method we present starts with the ECS model of Huber et al. (1992). We combine this predictive model with the best available thermodynamic equations of state. Furthermore, when thermal conductivity data are available, we use those data to fit a new "thermal conductivity shape factor" and/or a term in the traditional correlation for the dilute-gas portion of the thermal conductivity. This new model is analogous to our earlier work on viscosity (Klein et al. 1997).

METHOD

We follow the formalism of Ely and Hanley (1983) and Huber et al. (1992) who represent the thermal conductivity of a fluid as the sum of two parts—energy transfer due to translational and internal contributions

$$\lambda(T,\rho) = \lambda^{trans}(T,\rho) + \lambda^{\mathrm{int}}(T) \ , \tag{1}$$

where the superscript *trans* designates the translation term, i.e. contributions arising from collisions between molecules, and the superscript *int* designates the contribution from internal motions of the molecule. The internal term is assumed to be independent of density. The translation term is divided into a dilute-gas contribution λ^* and a density-dependent term, which is further divided into a residual part (superscript *r*) and a critical enhancement (superscript *crit*). The thermal conductivity is thus the sum of four terms:

$$\lambda(T,\rho) = \lambda^{\mathrm{int}}(T) + \lambda^{*}(T) + \lambda^{r}(T,\rho) + \lambda^{crit}(T,\rho) \ . \tag{2}$$

This paper focuses on the residual term which is the dominant contribution to the thermal conductivity of liquids and dense fluids away from the critical region. We adopt the standard formulas for the dilute-gas contributions which arise from kinetic theory and which have been used by Ely and Hanley (1983), Huber et al. (1992), and others, but with an empirical modification. We use an empirical approach to the critical enhancement. Each of these contributions is discussed in turn.

Dilute-Gas Contribution

The transfer of energy associated with internal degrees of freedom of the molecule is assumed to be independent of density and can be calculated using the Eucken correlation for polyatomic gases (Hirschfelder et al. 1967)

$$\lambda_j^{\mathrm{int}}(T) = \frac{f_{\mathrm{int}}\eta_j^{*}(T)}{M_j}\left[C_{P,j}^{\circ} - \frac{5}{2}R\right] , \tag{3}$$

where C_P° is the ideal-gas heat capacity, R is the gas constant, M is the molar mass, and η^* is the dilute gas viscosity. The subscript j emphasizes that all quantities are to be evaluated for fluid j.

The factor f_{int} in Equation (3) accounts for the conversion between internal and translational modes. It is a constant equal to 1×10^{-3} in the original Eucken correlation when R and C_P° are in J/(mol-K), η is in μPa.s, and λ is in W/m-K. Huber et al. (1992) use the value 1.32×10^{-3}, corresponding to the modified Eucken correlation. Reid et al. (1987) review this factor and state that even the value of 1×10^{-3} is too high for polar fluids. They review five different interpretations of f_{int}, but most of these involve quantities which are not available for many fluids. They also demonstrate that this factor has a weak, nearly linear, temperature dependence for a wide variety of fluids. In view of this, we take this factor to be an adjustable parameter and fit it to low-density experimental data as a linear function of temperature. In the absence of data, we use the constant 1.32×10^{-3}.

The dilute-gas part of the translational term is given by

$$\lambda_j^*(T) = \frac{15R\eta_j^*(T)}{4M_j} . \tag{4}$$

The dilute-gas viscosity appearing in Equations (3) and (4) is given by standard kinetic gas theory (Hirschfelder et al. 1967):

$$\eta_j^*(T) = 26.69\times10^{-3}\frac{\left(M_jT\right)^{1/2}}{\sigma_j^2\Omega^{(2,2)}\left(kT/\varepsilon_j\right)} \tag{5}$$

where σ_j and ε/k are the Lennard-Jones size and energy parameters, with units of nm and K, respectively, and $\Omega^{(2,2)}$ is the collision integral, which is a function of the temperature and ε/k. We use the empirical function of Neufeld (1972) for $\Omega^{(2,2)}$. While Equation (5) is derived from theory, the Lennard-Jones parameters are most often evaluated from low-density viscosity data. This function can thus be treated as a theoretically based correlating function.

Where experimentally based Lennard-Jones parameters are not available, they may be estimated by the relations suggested by Huber and Ely (1992):

$$\varepsilon_j/k = \varepsilon_0/k\frac{T_j^{crit.}}{T_0^{crit}} \text{, and} \tag{6}$$

$$\sigma_j = \sigma_0\left(\frac{\rho_0^{crit}}{\rho_0^{crit}}\right)^{1/3} , \tag{7}$$

where the subscript 0 refers to the reference fluid used in the extended corresponding states method described below.

Residual (Density-Dependent) Contribution

We use the principle of corresponding states to model the residual part of the thermal conductivity. Such models have been applied to a wide variety of fluids by many workers, including Leland and Chappelear (1968), Hanley (1976), Ely and Hanley (1983), and Huber et al. (1992). This approach is especially useful for fluids with limited experimental data.

The simple corresponding states model is based on the assumption that different fluids are conformal, that is they obey, in reduced coordinates, the same intermolecular force laws. (A reduced property is obtained by dividing by the corresponding critical point value.) This assumption leads to the conclusion that, with the appropriate scaling of temperature and density, the reduced residual Helmholtz energies and compressibilities of the unknown fluid "j" and a reference fluid "0" (for which an accurate, wide-ranging equation of state is available) are equal:

$$\alpha_j^r(T,\rho)=\frac{A_j(T,\rho)-A_j^\circ(T,\rho)}{RT}=\alpha_0^r(T_0,\rho_0) \quad , \tag{8}$$

and

$$Z_j(T,\rho)=Z_0(T_0,\rho_0) \quad . \tag{9}$$

The reference fluid is chosen to provide the best fit of the data and usually has a chemical structure similar to the fluid of interest.

The "conformal" temperature and density T_0 and ρ_0 defined by Equations 8 and 9 are related to the actual T and ρ of the fluid of interest by:

$$T_0=\frac{T}{f}=T\frac{T_0^{crit}}{T_j^{crit}\theta(T)} \quad , \tag{10}$$

and

$$\rho_0=\rho h=\rho\frac{\rho_0^{crit}}{\rho_j^{crit}}\phi(T) \ , \tag{11}$$

where the multipliers $1/f$ and h are termed equivalent substance reducing ratios, or simply "reducing ratios." Simple corresponding states was developed for spherically symmetric molecules for which the reducing ratios are simple ratios of the critical parameters (θ and ϕ both equal to 1). The extended corresponding states (ECS) model extends the method to other types of molecules by the introduction of the "shape factors" θ and ϕ. These shape factors are functions of temperature and density, although sometimes the density dependence is neglected.

The ECS method has been applied to both the thermodynamic and transport properties. By analogy with the thermodynamic properties, the thermal conductivity would be given by:

$$\lambda_j^r(T,\rho)=\lambda_0^r(T_0,\rho_0)\frac{\lambda_j\left(T_j^{crit},\rho_j^{crit}\right)}{\lambda_0\left(T_0^{crit},\rho_0^{crit}\right)} \tag{12}$$

But, the thermal conductivity goes to infinity at the critical point, and thus, another reducing parameter must be found. Evaluating the translational contribution given by kinetic theory (Equations 4 and 5) at the critical temperature yields

$$\lambda_j^*\left(T_j^{crit}\right)=\frac{C}{\sigma_j^2\Omega^{(2,2)}\left(T_j^{crit}k/\varepsilon_j\right)}\left(\frac{T_j^{crit}}{M_j}\right)^{1/2} , \tag{13}$$

where the gas constant and numerical constants in Equations (4) and (5) have been collapsed into the constant C. This reducing parameter has no physical meaning in itself, but it does have a reasonable theoretical basis.

Combining the reducing parameter defined in Equation (13) with Equation (12) yields:

$$\lambda_j^r(T,\rho)=\lambda_0^r(T_0,\rho_0)\left(\frac{T_j^{crit}}{T_0^{crit}}\right)^{1/2}\frac{\sigma_0^2\Omega^{(2,2)}\left(T_0^{crit}k/\varepsilon_0\right)}{\sigma_j^2\Omega^{(2,2)}\left(T_j^{crit}k/\varepsilon_j\right)}\left(\frac{M_0}{M_j}\right)^{1/2} \quad . \tag{14}$$

If the Lennard-Jones size parameter σ is taken to be proportional to the cube root of the critical volume, and the collision integrals $\Omega^{(2,2)}$ are assumed to be equal for fluid j and the reference fluid at their respective critical temperatures (reasonable assumptions in view of Equations 6 and 7) we obtain

$$\lambda_j^r(T,\rho) = \lambda_0^r(T_0,\rho_0)\left(\frac{T_j^{crit}}{T_0^{crit}}\right)^{1/2}\left(\frac{\rho_j^{crit}}{\rho_0^{crit}}\right)^{2/3}\left(\frac{M_0}{M_j}\right)^{1/2} . \tag{15}$$

Finally, if the ratios of critical parameters appearing in Equation (15) are replaced by the reducing ratios in Equations (10) and (11), we obtain

$$\lambda_j^r(T,\rho) = \lambda_0^r(T_0,\rho_0)F_\lambda , \tag{16}$$

where

$$F_\lambda = f^{1/2}h^{-2/3}\left(\frac{M_0}{M_j}\right)^{1/2} . \tag{17}$$

This result is equivalent to Equations (11) and (12) of Huber et al. (1992). Note that the dependence on the molecular masses is the inverse of the corresponding expression for viscosity (Equation 5 in Huber and Ely, 1992 or Equation 11 in Klein et al., 1997).

The shape factors (or, equivalently, the reducing ratios) may be obtained in several different ways. They can be fitted to experimental data, most often to vapor pressures and saturated liquid densities. Predictive methods exist which do not require any experimental data. In this work, we use the "exact shape factor" method where one equation of state is mapped onto another, that is, the conformal temperature and density which satisfy Equations (8) and (9) are found directly. The exact shape factor method implicitly assumes that accurate equations of state are available for both fluid j and the reference fluid.

Numerical solution of Equations (8) and (9) to find the reducing ratios is straightforward, in principle, but somewhat complicated in practice. At moderate and high densities a standard two-dimensional Newton's method iteration is used. The standard method is constrained in two ways. First, the derivative $(\partial P/\partial\rho)_T$ is calculated, and if it is negative (corresponding to a physically meaningless state) a different guess for density or temperature is generated. Second, the size of the temperature and density steps between iterations is limited. At low densities, this system tends towards a singularity, and a solution may not exist. If the Newton's method iteration fails, the quantity X, defined by

$$X = \left[\alpha_j^r(T,\rho) - \alpha_0^r(T_0,\rho_0)\right]^2 + \left[Z_j(T,\rho) - Z_0(T_0,\rho_0)\right]^2 , \tag{18}$$

is minimized. The density which minimizes X is found using a Brent's method parabolic interpolation scheme (Press et al. 1986). For each trial value of ρ_0 a secant method iteration is used to find the T_0 which satisfies Equation (8).

Modification of the Pure-Fluid ECS Method of Huber et al.

In view of the assumptions made in the ECS method, it is not apparent that the reducing ratios calculated from a thermodynamic equation of state should apply equally well to the transport properties. Klein et al. (1997) have shown that adjusting the conformal density by the addition of a viscosity shape factor improves the accuracy of the ECS method for that property. This approach can be extended to thermal conductivity as well by introducing a thermal conductivity shape factor χ defined by

$$\rho_0 = \chi h \rho , \tag{19}$$

where χ is a simple function of reduced density:

$$\chi = \sum_{k=0}^{n_k} c_k (\rho/\rho_c)^k \; . \tag{20}$$

The χ adjusts the conformal density at which the reference fluid thermal conductivity formulation is evaluated. If there were an exact correspondence between the thermodynamic properties and thermal conductivity, χ would be 1 for all fluids and at all conditions. We apply this new shape factor to a variety of fluids and demonstrate that values different from 1 improve the representation of experimental data.

Critical Enhancement

The thermal conductivity approaches infinity at the critical point, and even well removed from the critical point this "critical enhancement" can be a significant portion of the total thermal conductivity. Huber et al. (1992) apply the same multiplier F_λ to both the residual and critical enhancement parts of the reference fluid thermal conductivity. Although the theoretical basis for this approach is weak, it works fairly well on an empirical basis. They evaluate the critical enhancement at the same conformal temperature and density as the residual part. This has the small, but disconcerting, problem that the critical enhancement for fluid *j* will not peak at the critical point unless the shape factors are both 1.

To correctly locate the critical enhancement, we propose evaluating that term for the reference fluid at the same reduced temperature as the fluid of interest. In other words, for the critical enhancement only, the conformal temperature and density are

$$T_0^{c.e.} = \frac{T}{T_j^{crit}} T_0^{crit} \tag{21}$$

and

$$\rho_0^{c.e.} = \frac{\rho}{\rho_j^{crit}} \rho_0^{crit} \; , \tag{22}$$

where the superscript *c.e.* indicates that these conformal conditions apply only to the critical enhancement term.

While this modification correctly places the singularity in the thermal conductivity at the critical point it introduces a different problem. Far from critical, the simple reduced temperature and density are sometimes inside the two-phase boundary of the reference fluid, with the result that the critical enhancement is nonsense. (The reference fluid formulation we employ requires the evaluation of $(\partial P/\partial \rho)_T$, and this quantity can be zero or negative inside the two-phase region.)

To avoid both these problems, we propose the following method. The conformal conditions for the critical enhancement are the reduced conditions (Equations 21 and 22) at the critical point. For $0.8T^{crit} < T < 1.2\,T^{crit}$ and $0.6\rho^{crit} < \rho < 1.4\rho^{crit}$ they approach the "normal" conformal conditions (Equations 10 and 11) in a linear fashion. While this method is completely empirical, it does a reasonable job of representing the critical region data as demonstrated below.

Reference Fluid Formulation

Refrigerant 134a (1,1,1,2-tetrafluoroethane) was used in this work as the reference fluid. An extensive body of recent, high-quality experimental data is available for this fluid. It is a polar hydrofluorocarbon and is, thus, chemically similar to the other new HFC refrigerants, including R32, R125, and R143a. We use the recent R134a thermal conductivity surface of Perkins (1998), which is based on data measured in an IUPAC-sponsored evaluation (Assael 1995). The thermodynamic properties are calculated with the equation of state of Tillner-Roth and Baehr (1994).

RESULTS

Thermal conductivity values computed with the ECS method are compared to experimental values in Figures 1–3 for R12, R125, and ammonia. Although a major motivation for the ECS method is the calculation of properties for fluids with limited data, it is instructive to compare the method for fluids with extensive data sets available. In these three figures, the f_{int} and thermal conductivity shape factors are taken to be $1.32\text{x}10^{-3}$ and 1, respectively, corresponding to the Huber et al. (1992) method (except for a minor difference in the conformal conditions at which the critical enhancement is evaluated, as discussed above). For R12, this, the "traditional" ECS method, is seen to work very well. The deviations as $\rho \to 0$ are less than 4 %, but systematically negative, indicating that the modified Eucken correlation adequately describes the dilute-gas region, but could be improved by an optimized f_{int}. At high densities, the deviations are clustered about zero and their magnitudes are only slightly larger than the differences between different data sets. The deviations increase at densities near critical. The good quality of the fit is indicated by an overall average absolute deviation of 1.64%, where

$$AAD = \frac{1}{n_{points}} \sum_{k=1}^{n_{points}} 100 \left| \frac{\lambda_{calc} - \lambda_{exp}}{\lambda_{exp}} \right| . \tag{23}$$

For R125 (Figure C-2), the scatter at the dilute-gas limit is slightly larger. At higher densities, a systematic deviation of as much as 8% is seen. The overall AAD is 3.02%.

For ammonia (Figure C-3), the dilute-gas values are overpredicted by as much as 50%, confirming the statement of Reid et al. (1987) that the f_{int} in the Eucken correlation is too high for polar fluids. Near the critical density, a few points show deviations as high as 40%. At higher densities, the calculated values are consistently low by about 10%. The overall AAD is 17.4%.

The results for the "traditional" ECS method for a variety of fluids commonly used as refrigerants are summarized by the average absolute deviations given in the penultimate column of Table C-1. (The data sources used in this work were selected to cover a wide range of temperature and density. We feel that they are reliable sources, but the listing in Table 1 is not intended to be a comprehensive literature survey of the available data.) The HFCs, HCFCs, CFCs and ammonia considered here span a wide range of molecular weights and polarities, yet the traditional ECS method is seen to do a commendable job of representing thermal conductivity for most of these fluids. Even for ammonia, the fluid showing the largest deviations, the AAD of 17.4% is small considering that ammonia has a thermal conductivity as much as six times that of the reference fluid, and nearly half the overall AAD is due to a deficiency in the dilute-gas portion of the calculation. Recall that these results are not dependent on any experimental thermal conductivity values (apart from those underlying the reference fluid formulation).

When experimental data are available, they can be used to adjust the f_{int} and/or χ and improve the calculated values. For R125, the systematic underprediction at high densities can be avoided by adjusting the thermal conductivity shape factor χ. This was done by finding, for each data point, the value of χ which caused the calculated and experimental values of thermal conductivity to agree. (This was done using a Fibonnaci search technique.) The resulting values of χ are shown in Figure C-4. At high densities, the optimum χ are tightly clustered about an average value of about 1.03. At low densities, a huge scatter is seen. Several points did not converge at all and are plotted at the iteration bounds of 0 and 2. Since the χ shape factor affects

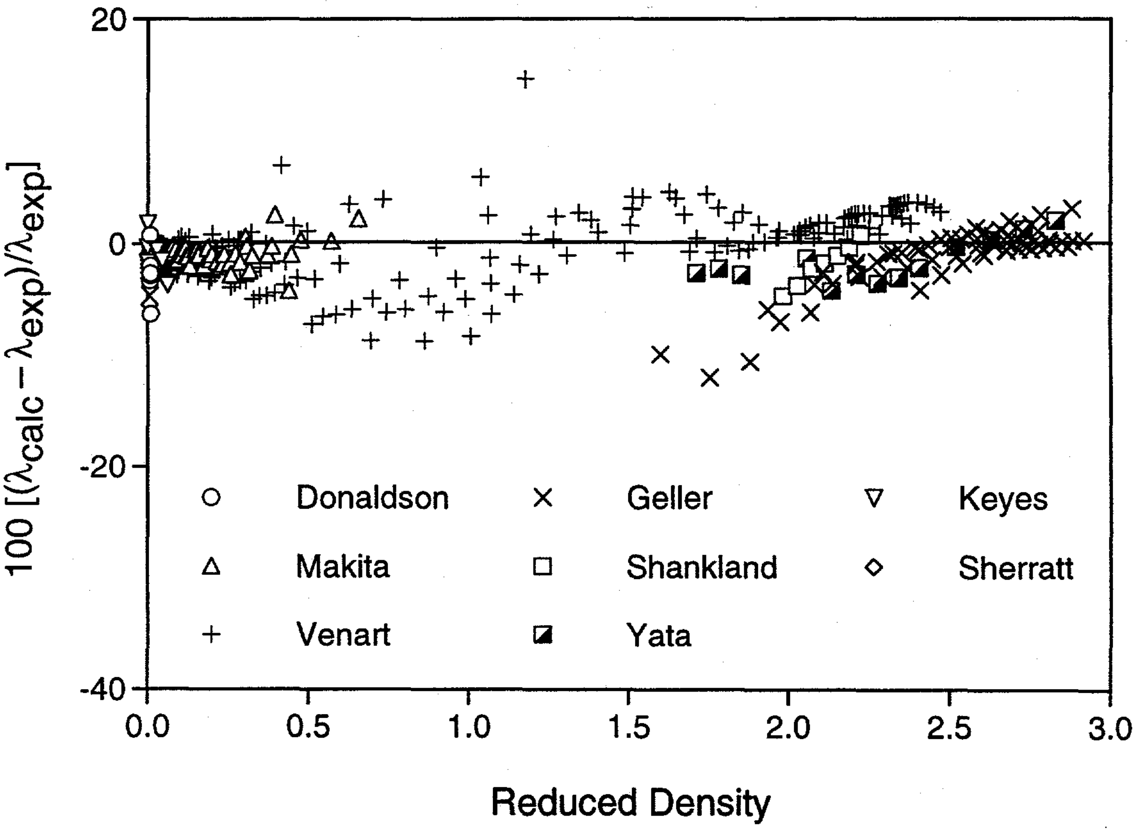

Figure C-1. Deviations between experimental thermal conductivity data for R12 and values calculated with the "traditional" ECS method [f_{int} = 1.32x10^{-3}, $\chi = 1$].

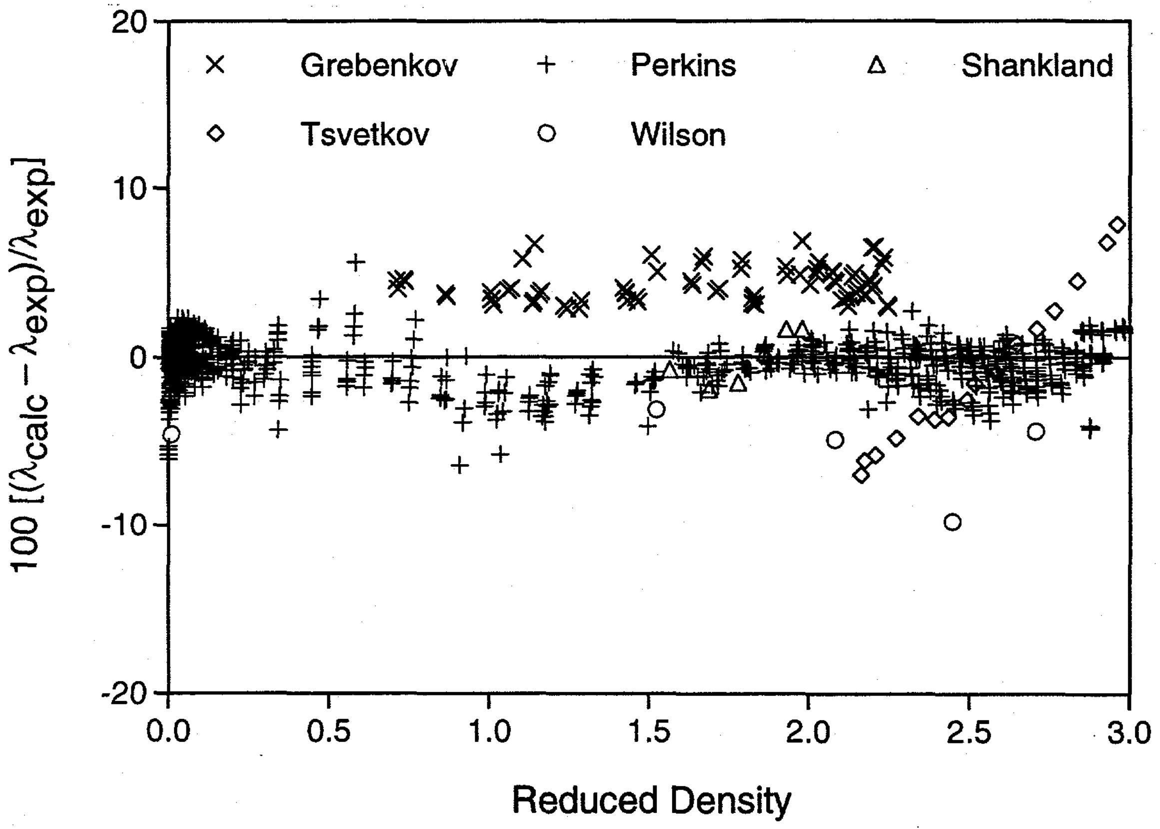

Figure C-2. Deviations between experimental thermal conductivity data for R125 and values calculated with the "traditional" ECS method [$f_{int} = 1.32 \times 10^{-3}$, $\chi = 1$].

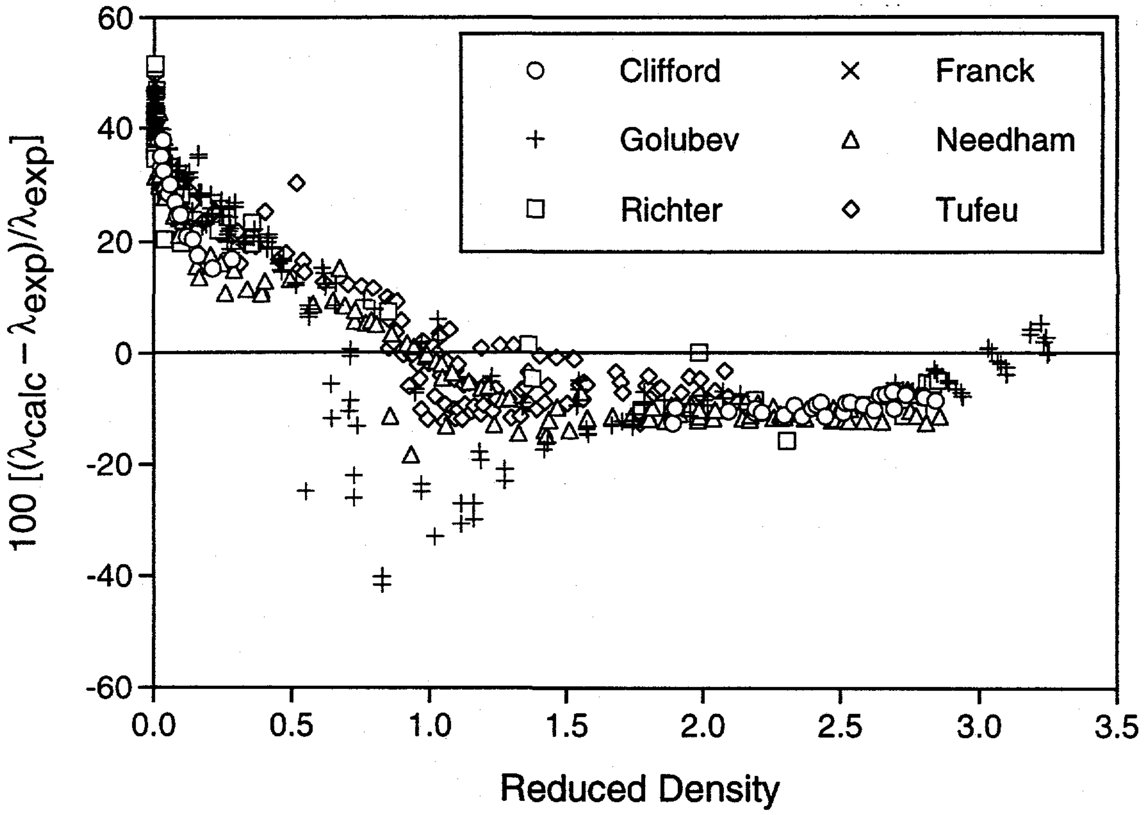

Figure C-3. Deviations between experimental thermal conductivity data for ammonia and values calculated with the "traditional" ECS method [f_{int} = 1.32x10^{-3}, χ = 1].

Table C-1. Data sources and average absolute deviations between experimental data and values computed with the "traditional" ECS method [$f_{int} = 1.32\times10^{-3}$, $\chi = 1$] and the present model [$f_{int} = f(T)$, $\chi = f(\rho/\rho^{crit})$].

Fluid	Equation of state source	Data source	No. points	Data range T (K)	Data range ρ/ρ^{crit}	AAD (%) traditional method	AAD (%) present model
ammonia	Tillner-Roth et al. (1993)	Clifford and Tufeu (1988)	40	296 – 387	0.025 – 2.84	15.20	3.16
		von Franck (1951)	7	275 – 584	0.0005 – 0.0011	42.32	1.85
		Golubev and Sololova (1964)	237	206 – 773	0.0012 – 3.25	21.41	4.52
		Needham and Ziebland (1965)	115	294 – 450	0.0038 – 2.86	13.87	4.25
		Richter and Sage (1964)	38	278 – 478	0.0020 – 2.85	22.16	4.81
		Tufeu et al. (1984)	122	381 – 578	0.016 – 2.09	10.88	5.19
		fluid totals	**559**	**199 – 773**	**0.0005 – 3.25**	**17.43**	**4.50**
R11	Jacobsen et al.(1992)	Richard and Shankland (1989)	6	305 – 328	0.0094 – 0.010	4.54	1.19
		Shankland (1990)	14	305 – 341	0.0094 – 2.62	3.78	0.96
		Yata et al.(1984)	12	233 – 438	1.84 – 2.93	4.26	1.16
		fluid totals	**32**	**233 – 438**	**0.0094 – 2.93**	**4.10**	**1.08**
R12	Marx et al.(1992)	Donaldson (1975)	6	277 – 347	0.0076 – 0.0096	2.98	2.18
		Geller et al. (1974)	65	193 – 373	1.60 – 2.92	1.81	1.86
		Keyes (1954)	7	323 – 423	0.0000 – 0.062	1.75	1.36
		Makita et al. (1981)	68	298 – 393	0.0066 – 0.66	0.99	0.73
		Shankland (1990)	13	303 – 343	0.0081 – 2.22	2.18	1.70
		Sherratt and Griffits (1939)	6	306 – 489	0.0053 – 0.0087	2.27	1.55
		Venart and Mani (1975)	204	300 – 600	0.0044 – 2.47	1.66	1.29
		Yata et al.(1984)	13	204 – 366	1.712 – 2.83	2.20	2.32
		fluid totals	**382**	**193 – 600**	**0.0000 – 2.92**	**1.64**	**1.36**
R13	Platzer et al. (1989)	Geller and Peredrii (1975)	78	213 – 433	0.0051 – 2.79	5.39	3.42
		Makita et al. (1981)	126	283 – 373	0.0059 – 1.56	6.60	3.27
		Yata et al.(1984)	4	204 – 264	2.05 – 2.57	0.79	2.35
		fluid totals	**208**	**204 – 433**	**0.0051 – 2.79**	**6.03**	**3.31**

Table 1. continued.

R22	Kamei et al.(1995)	Assael and Karagiannidis (1993)	37	253 – 333	1.98 – 2.67	5.22	0.73
		Donaldson (1975)	5	290 – 351	0.0058 – 0.0071	4.63	6.53
		Makita et al. (1981)	130	298 – 393	0.0051 – 1.30	3.32	1.99
		Shankland (1990)	4	312 – 342	1.87 – 2.16	2.08	3.42
		Tsvetkov and Laptev (1991)	134	313 – 411	0.0050 – 2.19	6.37	6.18
		Yata et al.(1984)	6	234 – 354	1.68 – 2.68	3.76	1.23
		fluid totals	**316**	**234 – 411**	**0.0050 – 2.68**	**4.85**	**3.70**
R23	ECS model in McLinden et al. (1998)	Geller and Peredrii (1975)	80	193 – 433	0.20 – 2.93	6.08	3.84
		Makita et al. (1981)	102	283 – 373	0.0000 – 0.78	4.16	1.45
		fluid totals	**182**	**193 – 433**	**0.0000 – 2.93**	**5.00**	**2.50**
R32	Tillner-Roth and Yokozeki (1997)	Grebenkov et al. (1994)	72	275 – 403	0.69 – 2.53	3.88	9.62
		Perkins et al. (1998)	1605	161 – 405	0.0017 – 3.35	10.51	3.17
		fluid totals	**1677**	**161 – 405**	**0.0017 – 3.35**	**10.23**	**3.45**
R114	Platzer et al. (1989)	Donaldson (1975)	4	304 – 343	0.011 – 0.012	9.29	9.27
		Keyes (1954)	3	323 – 423	0.0086 – 0.011	1.90	1.89
		Shankland (1990)	7	309 – 341	2.26 – 2.45	3.88	1.29
		Yata et al.(1984)	6	224 – 387	0.0000 – 2.59	3.00	1.19
		fluid totals	**20**	**224 – 423**	**0.0000 – 2.71**	**4.40**	**2.95**
R115	ECS model in McLinden et al. (1998)	Yata et al.(1984)	7	234 – 320	1.89 – 2.54	4.37	1.19
		Hahne et al. (1989)	163	290 – 369	0.021 – 2.22	7.06	5.76
		fluid totals	**170**	**234 – 369**	**0.021 – 2.54**	**6.95**	**5.57**
R125	Outcalt and McLinden (1995)	Grebenkov et al. (1994)	74	295 – 403	0.71 – 2.25	1.07	4.34
		Perkins et al. (1998)	978	192 – 392	0.0019 – 2.98	3.06	1.00
		Shankland (1990)	6	307 – 332	1.56 – 1.98	4.17	1.28
		Tsvetkov et al. (1993)	16	173 – 290	2.16 – 2.96	7.14	3.99
		Wilson et al. (1992)	7	216 – 333	0.0078 – 2.71	7.17	4.38
		fluid totals	**1081**	**173 – 403**	**0.0019 – 2.98**	**3.02**	**1.30**

Table 1. continued.

R142b	ECS model in McLinden et al. (1998)	Perkins et al. (1992)	56	302 – 304	2.53 – 2.87	4.45	0.89
		Sousa et al. (1992)	164	290 – 515	0.026 – 2.71	4.38	2.55
		Tanaka et al. (1991)	21	293 – 353	0.0088 – 0.14	1.55	1.76
		Yata et al. (1996)	24	251 – 333	2.35 – 2.93	6.84	1.91
		fluid totals	**265**	**251 – 515**	**0.0088 – 2.93**	**4.39**	**2.08**
R143a	Outcalt and McLinden (1997)	Perkins et al. (1998) (steady-state)	119	191 – 371	0.0001 – 0.095	6.68	1.91
		Perkins et al. (1998) (transient)	1125	191 – 373	0.0012 – 3.07	4.89	2.80
		Tanaka et al. (1991)	30	293 – 353	0.0067 – 0.58	7.27	14.01
		Yata et al. (1996)	24	268 – 314	2.07 – 2.64	9.64	4.00
		fluid totals	**1298**	**191 – 373**	**0.0001 – 3.07**	**4.49**	**3.00**

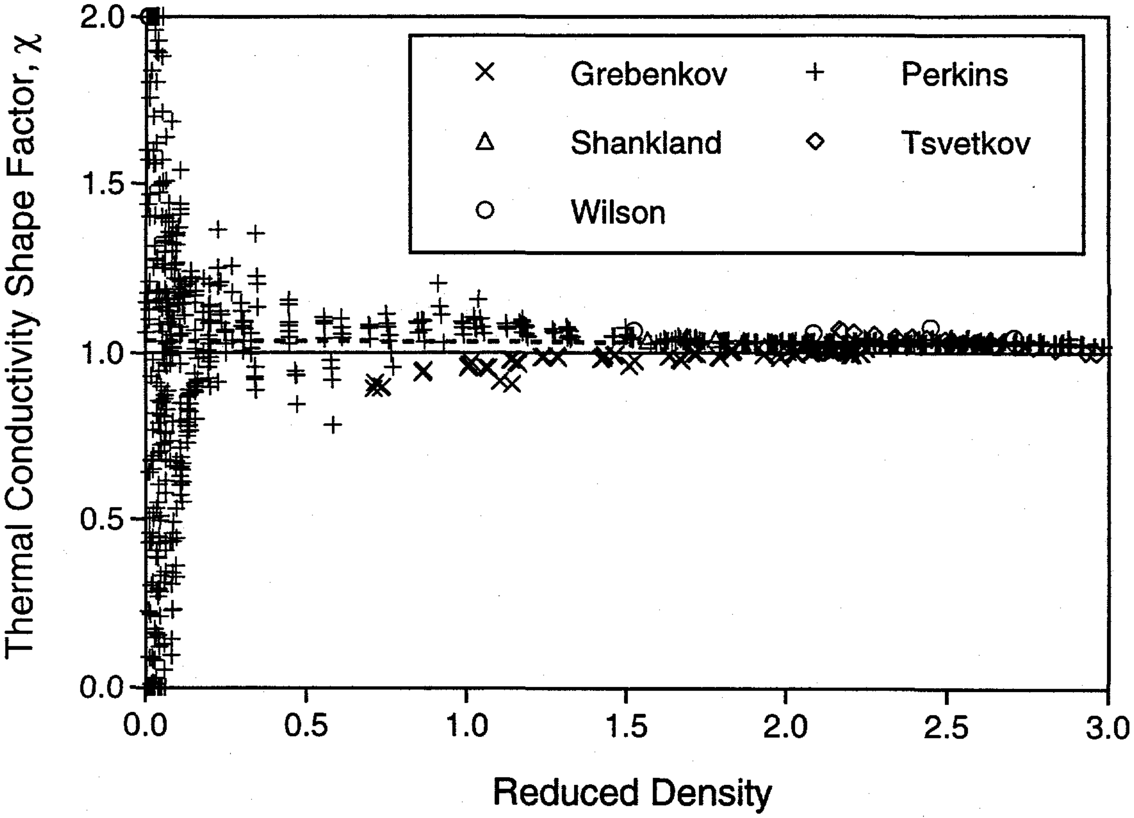

Figure C-4. Values of the thermal conductivity shape factor for R125 optimized for each data point. The solid line at $\chi = 1$ corresponds to the traditional ECS method; the dashed line is a least squares fit of the χ values at reduced densities > 1.

the residual part of the thermal conductivity, and at low densities, this term is a small fraction of the total, this scatter merely indicates that a large change in the residual term would be needed to compensate for small errors in the dilute-gas term. Using a χ which is a linear function of reduced density, together with an adjusted f_{int} results in the deviations shown in Figure C-5. The overall AAD has been reduced from 3.02% to 1.30%.

For ammonia, the optimum values of f_{int} were found in the same manner as that used for χ, except that only data points at $\rho/\rho^{crit} < 0.01$ were used. The resulting values of f_{int} were fit as a linear function of temperature, as shown in Figure C-6. Using this function for f_{int}, the optimum χ values were then found, and points at $\rho/\rho^{crit} > 1$ were fitted as a quadratic function of reduced density. The resulting deviations are shown in Figure C-7. The thermal conductivity is calculated over the full range of density with an AAD of 4.50%.

Refrigerant 12, which was represented very well by the traditional ECS method, and ammonia, which showed a dramatic improvement with the modified method, represent the extremes. Intermediate results were obtained for the other fluids considered. Table C-2 gives the optimized f_{int} functions as well as the values and sources for the Lennard-Jones parameters. Table C-3 gives the coefficients to the χ function (Equation 20). The final column in Table C-1 gives the AAD using these optimized functions for f_{int} and χ.

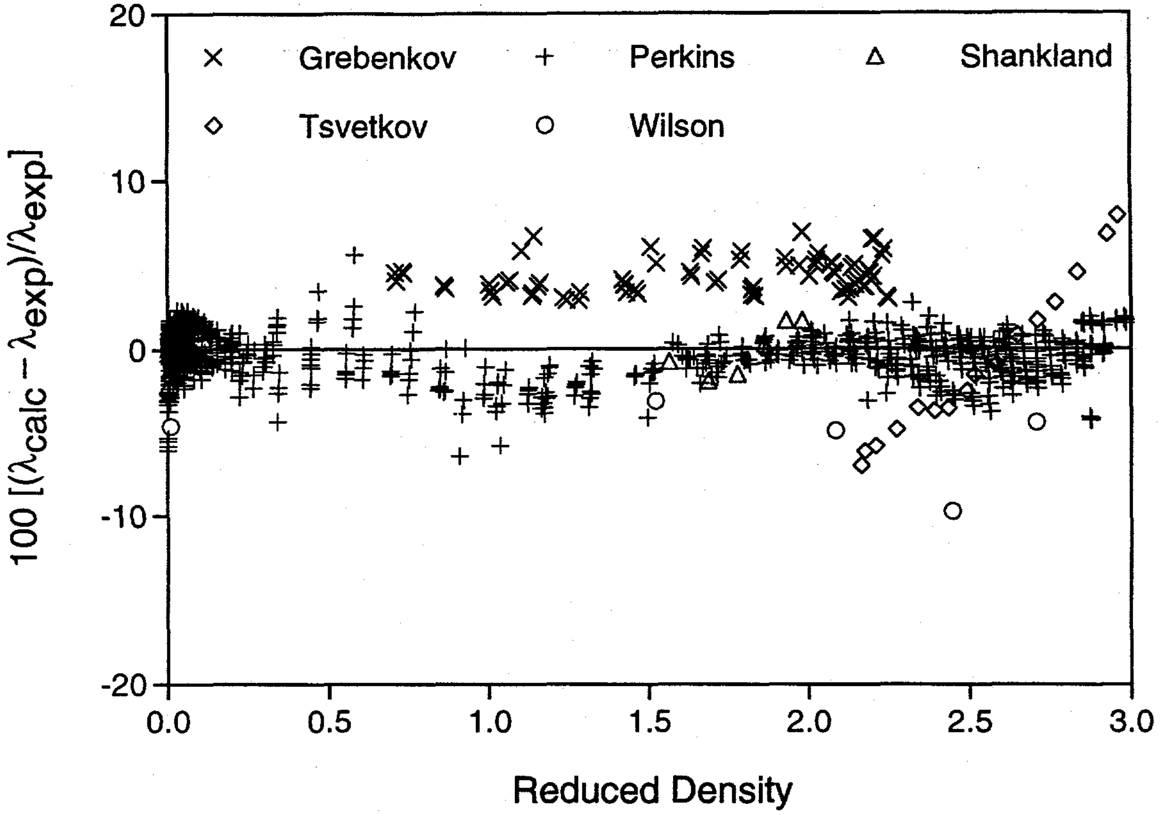

Figure C-5. Deviations between experimental thermal conductivity data for R125 and values calculated with the present ECS model [$f_{int} = f(T)$, $\chi = f(\rho/\rho^{crit})$].

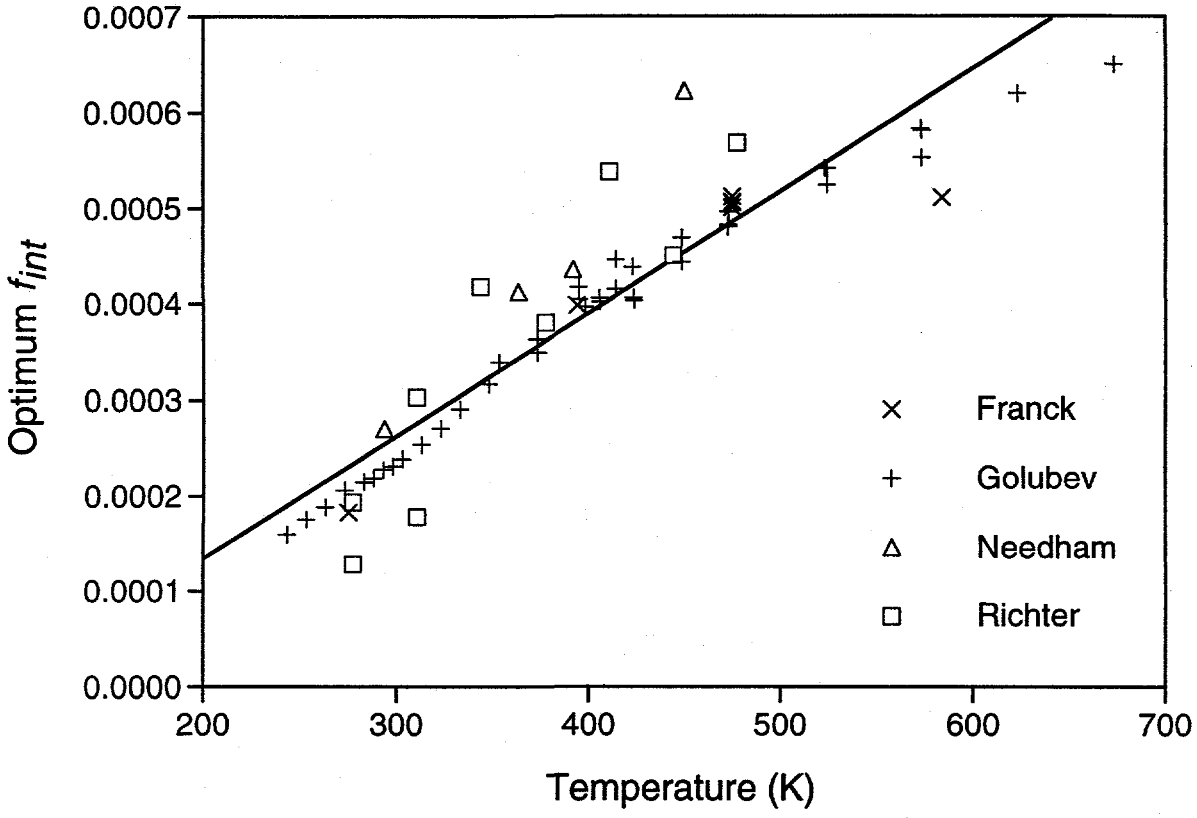

Figure C-6. Values of f_{int} optimized for individual data points for ammonia.

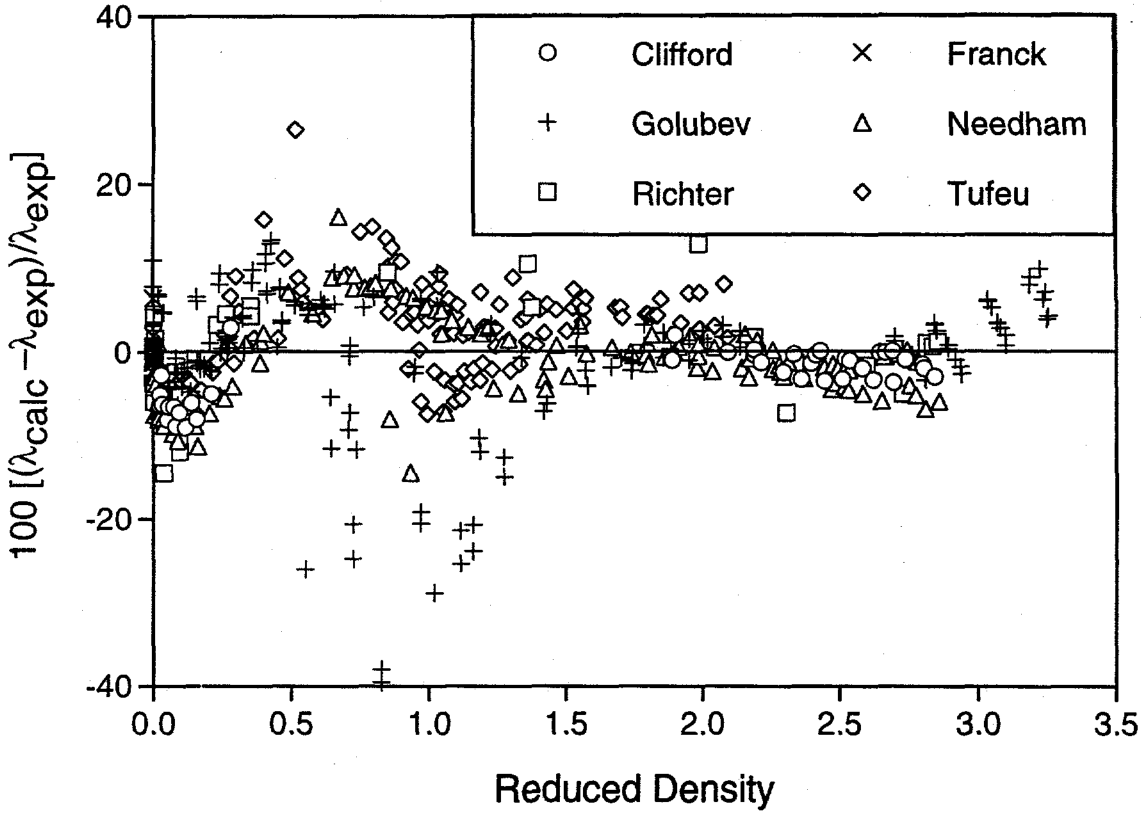

Figure C-7. Deviations between experimental thermal conductivity data for ammonia and values calculated with the present ECS model [$f_{int} = f(T)$, $\chi = f(\rho/\rho^{crit})$].

Table C-2. Parameters for the dilute-gas thermal conductivity.

Fluid	Lennard-Jones parameters source	σ (nm)	ε/k (K)	f_{int} in Eucken correlation (Equation 3) data source(s)	functional form (T in kelvins)
ammonia	Fenghour et al. (1995)	0.2957	386.00	Clifford and Tufeu (1988) von Franck (1951) Golubev and Sololova (1964) Needham and Ziebland (1965) Richter and Sage (1964)	$-1.2172\text{x}10^{-4} + 1.2818\text{x}10^{-6}T$
R11	[Eq. 6, 7]	0.5447	363.61	Richard and Shankland (1989)	$1.4000\text{x}10^{-3}$
R12	[Eq. 6, 7]	0.5186	297.24	Donaldson (1975) Keyes (1954) Makita et al. (1981) Shankland (1990) Sherratt and Griffits (1939) Venart and Mani (1975)	$1.3440\text{x}10^{-3}$
R13	[Eq. 6, 7]	0.4909	233.36	Geller and Peredrii (1975) Makita et al. (1981)	$1.3200\text{x}10^{-3}$
R22	Takahashi et al. (1983)*	0.4666	284.72	Donaldson (1975) Makita et al. (1981) Tsvetkov and Laptev (1991)	$7.7817\text{x}10^{-4} + 1.2636\text{x}10^{-6}T$
R23	[Eq. 6, 7]	0.4430	230.83	Makita et al. (1981)	$6.0570\text{x}10^{-4} + 1.8604\text{x}10^{-6}T$
R32	Takahashi et al. (1995)*	0.4098	289.65	Perkins et al. (1998)	$8.1980\text{x}10^{-4} + 2.2352\text{x}10^{-7}T$
R114	[Eq. 6, 7]	0.5770	323.26	Donaldson (1975) Keyes (1954)	$1.3200\text{x}10^{-3}$
R115	[Eq. 6, 7]	0.5476	272.53	Hahne et al. (1989)	$1.3200\text{x}10^{-3}$
R125	Assael et al. (1995)*	0.5101	261.39	Perkins et al. (1998) Wilson et al. (1992)	$1.2565\text{x}10^{-3} + 2.2296\text{x}10^{-6}T$
R142b	[Eq. 6, 7]	0.5320	316.64	Sousa et al. (1992) Tanaka et al. (1991)	$1.3200\text{x}10^{-3}$
R143a	[Eq. 6, 7]	0.5025	267.10	Perkins et al. (1998) Tanaka et al. (1991)	$1.0066\text{x}10^{-3} + 1.3729\text{x}10^{-6}T$

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*Lennard-Jones parameters fitted to the low-density viscosity data of the listed source.

Table C-3. Coefficients for the thermal conductivity shape factor (Equation 20); coefficients not listed are 0.

Fluid	c_0	c_1	c_2	c_3
ammonia	1.4312000	–0.2326400	0.0325210	
R11	1.0724000	–0.0226720		
R12	0.9910300	0.0029509		
R13	1.4078000	–0.2634600	0.0379780	
R22	1.0750000	–0.0385740		
R23	1.3801000	–0.2797500	0.0487980	
R32	1.2325000	–0.0883940		
R114	1.0961000	–0.0348990		
R115	1.0338000	–0.0020661		
R125	1.0369000	–0.0030368		
R142b	1.6808150	–0.8395440	0.3219570	–0.0397060
R143a	1.1779000	–0.2054100	0.0648700	–0.0064730

CONCLUSIONS

The traditional ECS method of Huber et al. (1992) was seen to work quite well in a purely predictive mode. The method predicted the thermal conductivities with an average absolute deviation of 7 % or less (compared to experimental data over wide ranges of temperature and density) for 10 of the 12 fluids studied. The R134a reference fluid used in this method was seen to work quite well for a variety of fluids, not just other HFCs. Somewhat surprising was that the weakly polar CFCs showed some of the smallest deviations, even though the R134a reference fluid is a highly polar HFC.

The present modification of the ECS method offers significant improvements over the traditional method when experimental thermal conductivity data are available. The relative improvement is greatest for highly polar fluids such as R32 and ammonia. Data at low densities are needed for polar fluids to fit the f_{int} factor in the Eucken correlation. Data at high densities are used to fit a new thermal conductivity shape factor, χ. With such data, the method yields deviations which are often comparable with the scatter in the data and the systematic differences between various data sources. The method reproduces experimental thermal conductivities with average absolute deviations of 4 % or less for 10 of the 12 fluids studied.

The critical enhancement is treated in an empirical way in the method. Further work on this contribution to the thermal conductivity is needed, but comparisons to data show that the present approach gives reasonable results.

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NOMENCLATURE

A	molar Helmholtz energy
AAD	average absolute deviation, defined in Equation
C	constant in Equation (13)
C_P°	ideal-gas heat capacity at constant pressure
f	equivalent substance reducing ratio for temperature
f_{int}	term in Eucken correlation for dilute-gas contribution
F_λ	multiplier for thermal conductivity, defined in Equation (17)
h	equivalent substance reducing ratio for density
M	molar mass
P	pressure
R	molar gas constant
T	absolute temperature
X	objective function for minimization defined in Equation (18)
Z	compressibility factor
α	reduced molar Helmholtz energy
χ	thermal conductivity shape factor
λ	thermal conductivity
ε/k	Lennard-Jones energy parameter
Φ	shape factor for density
$\eta*$	dilute-gas viscosity
ρ	molar density
σ	Lennard-Jones size parameter
θ	shape factor for temperature
$\Omega(2,2)$	collision integral

Subscripts

j	fluid of interest
r	reduced quantity
0	reference fluid
$\circ$	ideal-gas state

Superscripts

$c.e.$	critical enhancement
$crit$	critical point
id	ideal-gas state
int	thermal conductivity arising from internal motions
r	residual
t	translational part of thermal conductivity
$*$	dilute-gas part of translational term