

Thermodynamic properties for the alternative refrigerants*

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Models commonly used to calculate the thermodynamic properties of refrigerants are summarized. For pure refrigerants, the virial, cubic, Martin–Hou, Benedict–Webb–Rubin, and Helmholtz energy equations of state and the extended corresponding states model are discussed. High-accuracy formulations for 16 refrigerants are recommended. These models may be extended to mixtures through the use of mixing rules applied either to the parameters of the equation of state or to some property of the mixture components. Mixtures of a specific composition may also be modeled as a pseudo-pure fluid. Five mixture models, employing four distinct approaches, have been compared by a group working under the auspices of the International Energy Agency. These comparisons show all five models to be very capable in representing mixture properties. No single model was best in all aspects, but based on its combination of excellent accuracy and great generality, we recommend the mixture Helmholtz energy model as the best available.

Experimental data are essential to both fit the adjustable parameters in property models and to assess their accuracy. We present a survey of the data available for mixtures of the HFC refrigerants R32, R125, R143a, R134a, and R152a and for mixtures of the natural refrigerants propane, butane, isobutane, and carbon dioxide. More than 60 data references are identified. Further data needs include caloric data for additional mixtures, comprehensive pressure–density–temperature data for additional mixture compositions, and improved accuracy for vapor–liquid equilibria data. © 1998 Elsevier Science Ltd and IIR. All rights reserved.

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Les propriétés thermodynamiques de frigorigènes de remplacement

Les modèles souvent utilisés pour calculer les propriétés thermodynamiques de frigorigènes sont résumés. Pour les frigorigènes purs, les équations d'état du viriel, cubiques, de Martin-Hou, de Benedict-Webb-Ruben et de l'énergie de Helmholtz ainsi que les modèles d'état étendus correspondants sont exposés. Les formulations de haute précision pour 16 frigorigènes sont recommandées. Ces modèles peuvent être étendus aux mélanges en utilisant les règles de mélange qui s'appliquent directement aux paramètres de l'équation ou à une propriété des composants des mélanges. Les mélanges d'une composition spécifique peuvent être considérés comme un fluide quasi-pur. Cinq modèles de mélange employant quatre approches différentes ont été comparés par un groupe travaillant sous les auspices de l'Agence Internationale de l'Energie. Ces comparaisons montrent que les cinq modèles étudiés représentent fidèlement les propriétés de mélanges. Aucun modèle n'était le meilleur de tous les points de vue, mais étant donné la très grande précision et les applications très générales de modèle de l'énergie de Helmholtz, nous conseillons ce dernier comme le meilleur modèle disponible.

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a	equation of state energy parameter	x	composition (molar basis)
A	molar Helmholtz energy	y	parameter in CSD EOS
A_0, B_0, C_0	parameters in BWR EOS	Z	compressibility factor
A_1, B_1, C_1	parameters in Martin–Hou EOS	α	reduced molar Helmholtz energy and parameter in EOS
b	equation of state volume parameter	δ	dimensionless density in Helmholtz energy EOS
B	second virial coefficient	γ	EOS parameter
c	equation of state parameter	ρ	molar density
C	third virial coefficient	τ	dimensionless temperature in Helmholtz energy EOS
C_i	adjustable coefficient in Equation (41)	Φ, θ	shape factors in ECS model
C_p	heat capacity at constant pressure	β, ξ, ζ	adjustable parameters in mixture Helmholtz energy EOS
C_V	heat capacity at constant volume		
d_k	adjustable coefficient in Helmholtz energy EOS		
F_{pq}	generalizing parameter in mixture Helmholtz energy EOS		
f, g	parameters defined in eqns (8) and (9)		
f_j, h_j	equivalent substance reducing ratios in ECS model		
H	molar enthalpy		
K	parameter in Martin–Hou EOS		
k_T, k_V	adjustable parameters in mixture Helmholtz energy EOS		
k_{ij}, l_{ij}	binary interaction parameters		
l_k	adjustable coefficient in Helmholtz energy EOS		
n	number of components in a mixture		
N_i, N_k	adjustable coefficient in Helmholtz energy EOS		
P	pressure		
R	molar gas constant		
S	molar entropy		
t_i, t_k	numerical coefficient in Helmholtz energy EOS		
T	absolute temperature		
u, w	constants in cubic EOS		
w	speed of sound		
V	molar volume		

Les données expérimentales sont essentielles pour déterminer les paramètres ajustables dans les modèles de propriétés et pour évaluer leur précision. Nous présentons une revue des données disponibles concernant les mélanges de frigorigènes HFC R32, R125, R143a, R134a et R152a et pour les mélanges de frigorigènes naturels (propane, butane, isobutane et dioxyde de carbone). Plus de 60 références de données sont identifiées. Davantage de données, particulièrement des données caloriques pour des mélanges supplémentaires, des données sur les pressions, les densités et les températures pour des compositions de mélanges supplémentaires, ainsi qu'une précision accrue dans les données concernant l'équilibre vapeur-liquide, sont nécessaires. © 1998 Elsevier Science Ltd and IIR. All rights reserved. (Mots clés: frigorigène; mélange; propriétés thermodynamiques; equation d'état)

No one can doubt the importance of thermodynamic properties in the design of refrigeration equipment. Indeed, they are of such importance that a considerable

number of pages in reference works such as the ASHRAE *Handbook—Fundamentals*¹ are devoted to their tabulation. Refrigerant properties are invariably calculated with some sort of model—it is not possible to measure every property of interest at every combination

of temperature, pressure, and (in the case of mixtures) composition. In this paper, we give an overview of the models used to calculate the thermodynamic properties of refrigerants and refrigerant mixtures. This is not an exhaustive review; our intent is to highlight the approaches most commonly used for the refrigerants. Sources for high-accuracy formulations for the properties of pure refrigerants and a summary of the data available for some of the mixtures of current interest are also provided.

The thermodynamic properties include temperature, density, pressure, fugacity, internal energy, enthalpy, entropy, Gibbs and Helmholtz energies, heat capacities, speed of sound, chemical potential, and the Joule–Thompson coefficient as well as phase-equilibrium properties. They are distinguished from the transport properties of viscosity, thermal conductivity, and diffusion coefficient and the interfacial property of surface tension. The term ‘thermophysical properties’ includes all of the thermodynamic, transport, and interfacial properties.

Pure-fluid equations of state

An equation of state is a mathematical formulation of the thermodynamic properties of a fluid. A properly formulated equation of state, perhaps in combination with ancillary equations, is capable of reproducing experimental property data within the experimental uncertainty of the data over wide ranges of temperature and pressure. An equation of state is distinguished from a simple correlation of some individual property by its ability to yield, through integration and differentiation, all of the thermodynamic properties, including those (such as entropy) which cannot be directly measured.

An equation of state represents some thermodynamic property (usually pressure P , compressibility factor $Z = P/\rho RT$, or Helmholtz energy A) in terms of independent variables (almost always temperature T and density ρ [or its inverse, volume V], and, for mixtures, the composition). Given an equation of state explicit in P , Z , or A , all other thermodynamic quantities can be calculated by the appropriate manipulations. The starting point is the relationship between Helmholtz energy and pressure:

$$P = - \left(\frac{\partial A}{\partial V} \right)_T \quad (1)$$

If the equation of state is explicit in pressure, an integration is necessary:

$$A^r(T, \rho) = A - A^{\text{id}} = - \int_V^\infty (P - RT\rho) dV \quad (2)$$

This integration is carried out over the limits of the volume of interest and $V = \infty$, where the behavior of all fluids approaches the ideal gas limit. Thus arises the concept of a residual property—a property minus the corresponding property at an ideal-gas reference state.

The superscripts ‘r’ and ‘id’ refer to a residual quantity and the ideal-gas reference state. Other quantities arise by similar manipulations; for example, the residual entropy is given by

$$S - S^{\text{id}} = - \left(\frac{\partial (A - A^{\text{id}})}{\partial T} \right)_V \quad (3)$$

A pressure-explicit equation of state requires an ancillary equation for the heat capacity of the ideal-gas state for a complete description of the thermodynamic properties. An equation explicit in Helmholtz energy is usually written as the sum of residual and ideal-gas parts, and thus does not require an ancillary equation. See Younglove and McLinden² for a detailed discussion of the calculation of all properties from a pressure-explicit equation of state. Tillner-Roth and Baehr³ provide similar derivations for an equation in terms of Helmholtz energy.

The virial equation of state

Most practical equations of state are empirical and are fitted to experimental data. The virial equation of state, on the other hand, can be derived from statistical mechanics. This equation expresses the deviations from the ideal gas law as a power series in density

$$\frac{P}{\rho RT} = 1 + B\rho + C\rho^2 + D\rho^3 + \cdots \quad (4)$$

where the virial coefficients B , C , D , etc. are functions of temperature. Equation (4) reduces to the ideal-gas law at zero density. The second virial coefficient B accounts for the interactions resulting from collisions of two molecules; the third virial coefficient C accounts for three-body collisions, etc. The second and third virial coefficients may be derived from a variety of experimental measurements and are often available.

The virial equation of state is applicable only to vapor-phase properties. While, in principle, the virial equation would be applicable at all states, in practice, virial coefficients higher than third order are seldom available from experiment, and thus the virial equation is not practical for wide-range formulations. The second and third virial coefficients are usually sufficient to represent the vapor-phase properties of nonpolar gases up to about one-half the critical density. For polar fluids, such as the HFC refrigerants, the region of applicability is reduced.

Cubic equations of state

The cubic equations of state compose a class which includes many equations commonly used in industry. The original equation in this class was proposed by van der Waals in 1873:

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (5)$$

This equation introduced two corrections to the ideal-gas law:

- (1) an excluded volume expressed by the parameter b (the ideal-gas law assumes point masses); and
- (2) a long-range attractive force expressed by the parameter a (the ideal-gas law assumes no interactions).

The cubic equations of state may be expressed in the general form

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + ubV + wb^2}, \quad (6)$$

where the a and b parameters have the same interpretation as in Equation (5) and may be empirical functions of temperature fitted to experimental data or fixed functions of the critical temperature and/or pressure. The u and w are constants. Depending on the values of u and w and the functional form of the a and b parameters, Equation (6) represents the Peng–Robinson⁴, Soave–Redlich–Kwong⁵, or many other equations of state.

The cubic equations of state have the considerable advantage of yielding the density roots (given temperature and pressure) without iteration. This is accomplished by rearranging Equation (6) to yield a cubic polynomial (thus the name cubic equation of state) in the compressibility factor $Z = PV/RT$

$$Z^3 - (1 - ug + g)Z^2 + (f - ug - ug^2 + wg^2)Z - (fg + wg^2 + wg^3) = 0, \quad (7)$$

where

$$f = \frac{aP}{R^2T^2}, \quad (8)$$

and

$$g = \frac{bP}{RT}. \quad (9)$$

This advantage in computational speed comes at the expense of accuracy. The cubic equations are not capable of accurately representing properties over wide ranges of temperature and pressure. In particular, derived properties such as heat capacity and speed of sound in compressed liquid states have substantial error. Cubic equations can be used with good accuracy for vapor–liquid-equilibrium (VLE) calculations, that is, the computation of vapor pressures and, for mixtures, coexisting liquid and vapor compositions. Jacobsen et al.⁶ detail the limitations of the cubic equations of state as compared to a high-accuracy Helmholtz energy formulation. Nonetheless, if the region of interest is limited, and the fit of the equation has been optimized to data in that region, cubic equations can be used with good results.

Zhang et al.⁷ have proposed a new cubic equation of state where the van der Waals repulsive term is modified according to the hard-sphere model and an additional parameter c is used in the Redlich–Kwong-type attractive term in place of the excluded volume

parameter b :

$$P = \frac{RT}{V} \left(\frac{8V+3b}{8V-5b} \right) - \frac{a}{V(V+c)}. \quad (10)$$

The a , b , and c parameters are functions of reduced temperature. The addition of the c parameter significantly improves the accuracy of this equation over most other cubic equations. (This equation is compared to several other models in the Section 5 (Discussion)).

The Carnahan–Starling–DeSantis equation⁸, while not strictly a cubic equation of state (it is fifth-order in volume), is in the same spirit. It retains the attractive term of the cubic equations but replaces the simple excluded volume with a theoretical expression for the repulsive forces resulting from the collisions of hard spheres:

$$\frac{PV}{RT} = \frac{1+y+y^2-y^3}{(1-y^3)} - \frac{a}{RT(V+b)}, \quad (11)$$

where

$$y = b/4V. \quad (12)$$

The parameters a and b are empirical functions of temperature and have the same interpretation as in the cubic equations of state. The accuracy of the CSD equation is comparable to most other cubic equations of state.

The Martin–Hou equation of state

The Martin–Hou⁹ equation of state combines the van der Waals repulsive term with a much-expanded, empirical attractive term:

$$P = \frac{RT}{V-b} + \sum_{i=2}^5 \frac{A_i - B_iT + C_i \exp(-KT/T^{\text{crit}})}{(V-b)^i},$$

where K and the A_i , B_i and C_i are fitted parameters. (Note that some symbols used in this paper have multiple meanings; we sacrifice unique nomenclature to maintain consistency with the original sources.) As with the virial equation of state, the Martin–Hou equation is not valid in the liquid region. It is typically used with ancillary equations for the vapor pressure and saturated liquid density to calculate properties for saturated liquid states. The enthalpy of the saturated liquid is obtained from the vapor-phase properties and the ancillary equations by use of the Clapeyron equation

$$H_{\text{vap}} - H_{\text{liq}} = T(V_{\text{vap}} - V_{\text{liq}}) \frac{dP_{\text{sat}}}{dT}. \quad (14)$$

Downing¹⁰ provides an extensive discussion of this equation of state along with a compilation of the fitted parameters for many of the older refrigerants.

The BWR and MBWR equations of state

One of the earliest equations of state designed to cover wide ranges of conditions was introduced by Benedict,

Webb, and Rubin¹¹:

$$P = \rho RT + \left(B_0 RT - A_0 - \frac{C_0}{T^2} \right) \rho^2 + (bRT - a) \rho^3 + a\alpha\rho^6 + \frac{c\rho^3(1 + \gamma\rho^2)}{T^2} \exp(-\gamma\rho^2). \quad (15)$$

This equation has eight empirical constants A_0 , B_0 , C_0 , a , b , c , α , and γ . The first term on the right side of this equation yields the ideal-gas law. The next two groups of terms are analogous to the second and third virial terms. These terms provide proper behavior of the equation in the low-density vapor region. The final two groups of terms are empirical; the exponential function is used to fit the very steep isotherms in high-density compressed-liquid states.

The Benedict–Webb–Rubin (BWR) equation of state was modified and extended by Jacobsen and Stewart¹² to represent the properties of nitrogen. This modified Benedict–Webb–Rubin (MBWR) equation has subsequently been applied to a wide variety of fluids, including hydrocarbons, cryogenics, and refrigerants. 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 R123².

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

$$P = \sum_{i=1}^9 a_i \rho^i + \exp(-\rho^2/\rho_{\text{crit}}^2) \sum_{i=10}^{15} a_i \rho^{2i-17}, \quad (16)$$

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, like all pressure-explicit equations of state, 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 accuracy of these formulations varies, but uncertainties for R123 are typical: experimental data are reproduced with average absolute deviations of 0.04% for densities, 0.05% for vapor pressures, and 0.75% for heat capacities.

Helmholtz energy (fundamental) equations of state

Many recent high-accuracy pure-fluid equations of state have been expressed in terms of reduced molar Helmholtz energy using the general form:

$$\alpha = \frac{A}{RT} = \alpha^{\text{id}} + \alpha^{\text{r}} = \ln \delta - N \ln \tau + \sum_i N_i \tau^i + \sum_k N_k \tau^{t_k} \delta^{d_k} \exp(-\gamma \delta^{l_k}), \quad (17)$$

The first three terms on the right of Equation (17) constitute the ideal-gas contribution α^{id} . They are analogous to the combination of the a_1 term in the MBWR equation of state ($a_1 = RT$) and the ideal-gas heat capacity. The

ideal-gas contribution can also be represented by

$$\alpha^{\text{id}} = \frac{H_{\text{ref}}}{RT} - \frac{S_{\text{ref}}}{R} - 1 + \ln \left(\frac{T\rho}{T_{\text{ref}}\rho_{\text{ref}}} \right) + \frac{1}{RT} \int_{T_{\text{ref}}}^T C_p^{\text{id}} dT - \frac{1}{R} \int_{T_{\text{ref}}}^T \frac{C_p^{\text{id}}}{T} dT, \quad (18)$$

where H_{ref} and S_{ref} are an arbitrary reference enthalpy and entropy at the reference state specified by T_{ref} and ρ_{ref} .

The second summation in Equation (17) is the residual, or real-fluid, contribution α^{r} . The temperature and density are expressed in the dimensionless variables $\tau = T^*/T$ and $\delta = \rho/\rho^*$, where T^* and ρ^* are reducing parameters which are often, but not always, equal to the critical parameters. The N_i and N_k are numerical coefficients fitted to experimental data, and the exponents t_i , t_k , d_k and l_k are typically determined by a selection algorithm starting with a large bank of terms. The parameter γ is equal to 0 for terms with $l_k = 0$; it is equal to 1 for terms with $l_k \neq 0$. This ‘Helmholtz energy model’ is the basis for the international standard formulation for R134a³.

This model is sometimes termed a ‘fundamental equation’ because it gives a complete description of the thermodynamic properties, as discussed by Tillner-Roth and Baehr³. However, a pressure-explicit equation, such as the MBWR equation of state, combined with an equation for the ideal-gas heat capacity is entirely equivalent.

Extended corresponding states model

The extended corresponding states (ECS) model has been applied to the refrigerants by Huber and Ely¹³. It 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 property is reduced 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:

$$\alpha_j^{\text{r}}(T_j, \rho_j) = \alpha_0^{\text{r}}(T_0, \rho_0), \quad (19)$$

and

$$Z_j(T_j, \rho_j) = Z_0(T_0, \rho_0). \quad (20)$$

When combined with an expression for the ideal-gas heat capacity, all other thermodynamic properties can be calculated. The reference fluid is evaluated at a ‘conformal’

temperature and density:

$$T_0 = \frac{T_j}{f_j} = T_j \frac{T_0^{\text{crit}}}{T_j^{\text{crit}} \theta(T)}, \quad (21)$$

and

$$\rho_0 = \rho_j h_j = \rho_j \frac{\rho_0^{\text{crit}}}{\rho_j^{\text{crit}}} \phi(T) \quad (22)$$

where the multipliers $1/f_j$ and h_j are termed equivalent substance reducing ratios. Simple corresponding states was developed for spherically symmetric molecules for which the reducing ratios are simple ratios of the critical parameters. The 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 shape factors 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. The 'exact shape factor' method maps one equation of state onto another; this method is usually used when the ECS method is used for mixture calculations. The reference fluid is chosen to provide the best fit of the data and has a chemical structure similar to the fluid of interest.

Equations of state for mixtures

Equations of state for refrigerant mixtures are usually the result of one of three basic approaches:

- (1) Calculation of properties of a mixture at a specific composition as a pseudo-pure fluid.
- (2) Application of mixing rules to parameters in the constituent pure-fluid equations of state.
- (3) Application of mixing rules to some property of the constituent pure fluids.

Pseudo-pure-fluid approach

The approach to modeling mixture properties traditionally taken in the refrigeration industry treats a mixture of a specific composition as a pseudo-pure fluid. This approach has worked in the past because the mixtures of interest were mostly azeotropes, that is, the 500-series refrigerants which behave essentially like pure fluids in that the compositions of the liquid and vapor phases are nearly equal and isobaric (constant pressure) evaporation and condensation take place at a constant temperature. The R502 formulation by Martin and Downing¹⁴ using the Martin-Hou equation of state is a classic example. The major advantages of this approach are simplicity and compatibility with computer programs which may have been originally developed for pure fluids. The major disadvantage is that accounting for the variations of properties with composition is not possible. Even mixtures that form azeotropes will exhibit differing liquid and vapor compositions at some conditions, and

blending tolerances in manufacture may result in an 'azeotropic mixture' that is, in fact, not an azeotrope.

Mixing rules applied to EOS parameters

Pure fluid equations of state can be extended to mixtures by defining a set of parameters applicable to the mixture. This approach is generally successful only when the EOS parameters have a physical interpretation. For the virial equation of state, the mixing rules for the virial coefficients are defined by statistical mechanics:

$$B_{\text{mix}} = \sum_{i=1}^n \sum_{j=1}^n x_i x_j B_{ij}, \quad (23)$$

$$C_{\text{mix}} = \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n x_i x_j x_k C_{ijk}, \text{ etc.} \quad (24)$$

The B_{ii} and C_{iii} (e.g. B_{11} , B_{22} , C_{111} , C_{222}) are the virial coefficients for the pure components. The cross terms B_{ij} and C_{ijk} (where i , j , and k are not all the same number) represent interactions between unlike molecules. These cross terms cannot be determined from the properties of the pure substances; they are usually determined from experimental mixture (P - ρ - T) data. The applicability of the virial equation of state for mixtures is subject to the same limitations as for pure fluids.

A similar approach is taken with the cubic equations of state. While the details vary among the many cubic equations of state which have been proposed, the approach most often taken can be generally described as follows. The energy and volume parameters for the mixture are defined as

$$a_{\text{mix}} = \sum_{i=1}^n \sum_{j=1}^n x_i x_j a_{ij}, \text{ and} \quad (25)$$

$$b_{\text{mix}} = \sum_{i=1}^n \sum_{j=1}^n x_i x_j b_{ij}. \quad (26)$$

The cross terms for the energy parameter a_{ij} are usually given by the geometric mean of the pure component parameters

$$a_{ij} = (1 - k_{ij}) (a_i a_j)^{1/2}, \quad (27)$$

where the k_{ij} are 'binary interaction parameters' which are fitted to experimental mixture data, most often vapor-liquid-equilibria (VLE) data. The k_{ij} parameters may be functions of temperature and/or composition. The b parameter is given by the arithmetic mean of the 'volume' or the 'diameter':

$$b_{ij} = \frac{1}{2} (b_i + b_j), \text{ or} \quad (28)$$

$$b_{ij} = \frac{1}{8} (b_i^{1/3} + b_j^{1/3})^3. \quad (29)$$

A binary interaction parameter is sometimes also applied to the volume parameter in addition to the energy parameter. The properties of mixtures with three or more components are usually modeled only in terms of

the constituent binary pairs. Relatively few cubic equations account for interactions between three or more components.

This approach, especially as applied to the cubic equations of state, has the advantage of simplicity—often only a single empirical parameter is used to describe a binary pair—and is thus well suited to mixtures with limited experimental data. Furthermore, if the EOS parameters have a solid physical interpretation, binary interaction parameters can be estimated with reasonable success. (See, for example, the method of Morrison and McLinden¹⁵ for the Carnahan–Starling–DeSantis equation of state.) This method carries with it any limitations of the underlying pure fluid equation of state. It is also necessary that all components in a mixture be modeled in terms of the same equation of state. Since high-accuracy equations of state are available for many refrigerants, use of this mixture approach would sacrifice the accuracy of the best pure fluid equations for many fluids. In addition, if separate high-accuracy equations were used for pure-fluid calculations, mixture properties calculated by this model as the composition approached 1 would not be consistent with the pure-fluid properties.

The extended corresponding states model for mixtures

The ECS model of Huber and Ely¹³ can be extended to mixtures. The method is based on the equality of the compressibility factor and reduced residual Helmholtz energy formulations as previously stated in eqns (19) and (20). The reducing ratios for the mixture are determined from those of the constituent pure components by the standard van der Waals one-fluid mixing rules:

$$h_{\text{mix}} = \sum_{i=1}^n \sum_{j=1}^n x_i x_j h_{ij}, \text{ and} \quad (30)$$

$$f_{\text{mix}} h_{\text{mix}} = \sum_{i=1}^n \sum_{j=1}^n x_i x_j f_{ij} h_{ij}, \quad (31)$$

where the cross terms (indicated by the subscript ij) are computed using the combining rules

$$f_{ij} = \sqrt{f_i f_j} (1 - k_{ij}), \text{ and} \quad (32)$$

$$h_{ij} = \frac{1}{8} (h_i^{1/3} + h_j^{1/3})^3 (1 - l_{ij}). \quad (33)$$

The k_{ij} and l_{ij} are binary interaction parameters which are fitted to experimental data. This method is seen to be a variation of the general approach of applying mixing rules to the EOS parameters.

Mixing rules applied to the Helmholtz energy

A new model which was developed, in slightly different forms, independently by Lemmon¹⁶ (also described by Lemmon and Jacobsen¹⁷) and Tillner-Roth¹⁸, calculates the thermodynamic properties of mixtures by applying mixing rules to the Helmholtz energy of the mixture

components:

$$\alpha_{\text{mix}} = \sum_{j=1}^n [x_j (\alpha_j^{\text{id}} + \alpha_j^{\text{r}}) + x_j \ln x_j] + \sum_{p=1}^{n-1} \sum_{q=p+1}^n x_p x_q F_{pq} \alpha_{pq}^{\text{excess}}. \quad (34)$$

This mixing formula may be applied directly to Helmholtz energy equations of state. Application to the MBWR equation of state requires the transformation previously expressed in Equation (2). The first summation in this equation represents the ideal solution; it consists of ideal gas (superscript 'id') and residual or real fluid (superscript 'r') terms for each of the pure fluids in the n -component mixture. The $x_j \ln x_j$ terms arise from the entropy of mixing of ideal gases where x_j is the mole fraction of component j . The double summation accounts for the 'excess' Helmholtz energy or 'departure' from ideal solution. The F_{pq} are generalizing parameters which relate the behavior of one binary pair with that of another; F_{pq} multiplies the $\alpha_{pq}^{\text{excess}}$ term(s), which are empirical functions fitted to experimental binary mixture data. The α_j^{r} and $\alpha_{pq}^{\text{excess}}$ functions in Equation (34) are not evaluated at the temperature and density of the mixture T_{mix} and ρ_{mix} but, rather, at a reduced temperature and density τ and δ . These τ and δ parameters are very much in the spirit of the conformal temperature and density of the ECS method and are a key feature in this model. The mixing rules for the reducing parameters are

$$\tau = \frac{T^*}{T_{\text{mix}}}, \text{ with } T^* = \sum_{p=1}^n \sum_{q=1}^n k_{T,pq} x_p x_q \frac{1}{2} (T_p^{\text{crit}} + T_q^{\text{crit}}), \quad (35)$$

and

$$\delta = \frac{\rho_{\text{mix}}}{\rho^*}, \text{ with } \frac{1}{\rho^*} = \sum_{p=1}^n \sum_{q=1}^n k_{V,pq} x_p x_q \frac{1}{2} \left(\frac{1}{\rho_p^{\text{crit}}} + \frac{1}{\rho_q^{\text{crit}}} \right). \quad (36)$$

Alternate forms which combine the $k_{T,pq}$ with the critical temperatures and the $k_{V,pq}$ with the critical densities are also used:

$$\frac{1}{\rho^*} = \sum_{p=1}^n x_p \frac{1}{\rho_p^{\text{crit}}} + \sum_{p=1}^{n-1} \sum_{q=p+1}^n \xi_{pq} x_p x_q, \quad (37)$$

and

$$T^* = \sum_{p=1}^n x_p T_p^{\text{crit}} + \sum_{p=1}^{n-1} \sum_{q=p+1}^n \zeta_{pq} x_p^{\beta_{pq}} x_q. \quad (38)$$

If only limited vapor–liquid equilibrium (VLE) data are available, the $\alpha_{pq}^{\text{excess}}$ term is taken to be 0, and only the $k_{T,pq}$ and/or $k_{V,pq}$ parameters are fitted. The $k_{T,pq}$ parameter is most closely associated with bubble-point pressures, and it is necessary to reproduce azeotropic behavior. The $k_{V,pq}$ parameter is associated with volume changes on mixing. Ternary and higher-order

mixtures are modeled in terms of their constituent binary pairs ($k_{T,pq} = 1$ and $k_{V,pq} = 1$ for $p = q$). If mixture data, including single-phase pressure–density–temperature (P – ρ – T) and possibly heat-capacity data, are available, the $\alpha_{pq}^{\text{excess}}$ function can be determined. The F_{pq} parameter is used (either alone or in combination with $k_{T,pq}$ and $k_{V,pq}$) to generalize the detailed mixture behavior described by the $\alpha_{pq}^{\text{excess}}$ function to other binaries. Lemmon¹⁶ has determined a generalized $\alpha_{pq}^{\text{excess}}$ function based on data for 28 binary pairs of hydrocarbons, inorganic molecules (including carbon dioxide), and HFCs.

This ‘mixture Helmholtz energy 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 approach exactly those of the pure components as the composition of any constituent approaches a mole fraction of 1. Different components in a mixture may be modeled with different forms; for example, an MBWR equation may be mixed with a Helmholtz energy equation of state. If the components are modeled with the ECS method, this mixture model allows the use of a different reference fluid for each component. 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.

Mixing rules applied to other properties

Piao et al.¹⁹ modeled the properties of binary and ternary mixtures of R32, R125, and R134a by applying mixing rules to the pressure. They used an 18-term modified Benedict–Webb–Rubin equation of state expressed in terms of reduced pressure, temperature, and density. The critical parameters of the mixture are given by empirical functions. The reduced pressure of the mixture is then given by

$$P_{r,\text{mix}} = x_1 P_{r,1} + x_2 P_{r,2} + x_3 P_{r,3} + k_{\text{mix}} P_r^E \quad (39)$$

where the $x_i P_{r,i}$ are the terms from the corresponding pure fluid equations. The $k_{\text{mix}} P_r^E$ term represents the departure from ideal mixing. The k_{mix} is an empirical function of composition and the P_r^E is an empirical function of temperature and density. A total of more than 50 adjustable parameters (in addition to the pure component parameters) are used to model this ternary system and its three constituent binaries. This model is compared to others in Section 5 (Discussion).

Hybrid approaches

Separate equations can be used to model different regions or properties. We will call these hybrid

models. The motivation for using a hybrid approach is usually to:

- (1) simplify the calculation of properties and decrease the computational time required; or
- (2) to compensate for a weakness in the functional form of the equation of state.

As examples of the first motivation, the extended corresponding states model of Huber and Ely¹³ and the pressure-explicit model of Piao et al.¹⁹ use the Peng–Robinson cubic equation of state to solve for the vapor–liquid equilibria, that is, the pressure and coexisting compositions of two-phase states at a specified temperature. Given the temperature, pressure, and composition, the primary EOS is then used to solve for the density and all other thermodynamic properties.

An example of the second motivation is given by Yokozeki²⁰, who has developed a model for refrigerant mixtures which relies heavily on the hybrid approach to compensate for the deficiencies usually encountered with cubic equations of state. He starts with the van der Waals equation of state (Equation (5)) with the molar volume modified by an additional parameter c :

$$P = \frac{RT}{V + c - b} - \frac{a_c \alpha}{(V + c)^2} \quad (40)$$

The parameters a_c , b , and c are constants for a given pure fluid and α is an empirical function of temperature. The usual mixing rules are applied to arrive at the corresponding parameters for the mixture. Equation (40) is combined with an ancillary equation for the ideal-gas heat capacity:

$$C_p^{\text{id}} = C_0 + C_1 T + C_2 T^2 + C_3 T^3 \quad (41)$$

Thus far, this is the standard approach for any cubic equation of state. But Yokozeki fits one set of parameters for Equation (40) for application to vapor–liquid equilibrium calculations and another set of parameters for use in calculating densities in the vapor-phase. The equation for entropy is derived using the usual relations

$$S = R \ln \frac{P_{\text{ref}}}{RT} (V - b) + \frac{a_c}{V} \frac{\partial \alpha}{\partial T} + \int_{T_{\text{ref}}}^T \frac{C_p^{\text{id}}}{T} dT + S_{\text{ref}} \quad (42)$$

where the entropy S is relative to a reference state entropy S_{ref} at the temperature and pressure T_{ref} and P_{ref} . But when applied to liquid-phase calculations, $\partial \alpha / \partial T$ in this equation is not the derivative of α appearing in Equation (40), but a separate empirical function. Furthermore, separate functions are used for the ideal-gas heat capacity in the liquid and vapor phases. The isochoric heat capacity is computed using the second partial derivative of the pressure with respect to the temperature. For the present equation, this takes the form

$$C_V = C_p^{\text{id}} - R + T \int_{\infty}^V \left(\frac{\partial^2 P}{\partial T^2} \right)_V = C_p^{\text{id}} - R + T \int_{\infty}^V \left(a_c \frac{\partial^2 \alpha}{\partial T^2} \right)_V \quad (43)$$

Again, a separate empirical function is used for the derivative when the above equation is used for liquid-phase calculations. While Yokozeki²⁰ admits that the "present model may at first seem cumbersome and complicated," he demonstrates that it represents the properties of R32, R125, and their mixtures very well. Furthermore, by fitting the separate functions to discrete properties, Yokozeki argues that the determination of the numerical coefficients is simplified and requires fewer experimental data than the common high-accuracy equations of state.

The use of multiple equations in the hybrid approaches will result in properties which are not strictly thermodynamically consistent. With care, these inconsistencies can be minimized and such models have been used quite successfully. Nevertheless, philosophies differ, and we prefer a simultaneous fitting of multiple properties to arrive at a single equation of state which will allow the calculation of all the thermodynamic properties.

Availability of mixture data

Experimental data are paramount in any consideration of fluid thermophysical properties. Data are necessary for fitting the adjustable parameters present in most mixture models. Furthermore, the quality of a model is assessed by comparing calculated values with experimental data. Vapor-liquid-equilibrium (VLE) data consist of the pressure at saturation, the coexisting liquid and vapor compositions, and sometimes also the coexisting liquid and vapor densities. VLE data are the most important for refrigeration applications where processes are usually close to saturation. Refrigeration systems using the new high-pressure HFC mixtures operate much closer to the critical point than traditional R12 and R22 systems. Many models are not as accurate near the critical point so VLE data are especially important in this region for assessing the validity of a model. Pressure-density-temperature (P - ρ - T) data in single-phase states are the most important data for fitting away from the saturation boundary. While caloric properties, such as constant volume and constant pressure heat capacities C_V and C_P and speed of sound w , can be predicted by an equation of state, experimental caloric data are invaluable for validating a property model.

We present in *Table 1* a survey of the available data for mixtures of the HFCs R32, R125, R143a, and R134a along with mixtures of carbon dioxide, propane, butane, and isobutane. Only published data and, in a few cases, results which will be published soon are included. Additional work is in progress at a number of university, government, and industrial laboratories, and other unpublished work exists, particularly from industry. These systems include the commercial mixtures R404A, R407C, R410A, and R507A. (R404A is the mixture of R125, R143a, and R134a with a composition of 44, 52, and 4 mass percent, respectively; in standard ASHRAE nomenclature this is expressed as R125/143a/134a (44/52/4). R407C is R32/125/134a (23/25/52), R410A is R32/125 (50/50), and R507A is the azeotropic mixture

R125/143a (50/50).) Numerous VLE and P - ρ - T data sets are available for most of these mixtures, although some are very restricted in their temperature, pressure, and/or composition ranges. There are also wide variations in the quality of the data. While most of the recent measurements are of high quality, many of the data on the mixtures of the natural refrigerants are quite old. There are also sometimes large differences between VLE data sets. The most striking limitation of the present data apparent from this survey is the paucity of caloric data. Such data are listed for just four of the mixtures examined, and usually only one composition has been measured for each system.

Discussion—the evaluations of IEA Annex 18

In view of the existence of multiple approaches to the important problem of representing the thermodynamic properties of the new refrigerants and their mixtures, as well as those of the long-recognized natural refrigerants such as ammonia, carbon dioxide, and the simple hydrocarbons, it is desirable to select standard formulations for use by the refrigeration industry. This task has been taken on by a group working under the auspices of the Heat Pump program of the International Energy Agency. Eight member countries (Austria, Canada, Germany, Japan, Norway, Sweden, the United Kingdom, and the United States) have joined together to form Annex 18—Thermophysical Properties of the Environmentally Acceptable Refrigerants. One of the goals of this Annex (or program working group) is to evaluate the available models and recommend formulations as international standards.

Thus far, IEA Annex 18 has evaluated pure-fluid equations of state for R123, R134a, R32, and R125. The evaluation process has been described by Penoncello et al.⁸⁶. A similar evaluation is under way for R143a. *Table 2* gives references for the equations of state recommended by Annex 18 as well as additional high-accuracy equations for other refrigerants, including ammonia, carbon dioxide, and the hydrocarbon refrigerants. Most of these sources also include detailed surveys of the experimental data used to develop the equations. These formulations will yield the most accurate thermodynamic properties available for these fluids at this time. This is not to say, however, that these formulations are the final word on the subject or even the only valid approach currently available. There are gaps in the data for even these highly studied HFCs (especially for R125). As more data are measured, these formulations are sure to be improved upon. But the present standards should serve as the benchmark. Any new equation of state should offer some improvement, either demonstrably superior accuracy or greater simplicity with comparable uncertainties (at least over some range of conditions).

The high-accuracy models recommended by the Annex come at a price: slow speed of calculation. While the slow speed of these models is of little consequence in computing a table of a few dozen points,

Table 1 Summary of experimental data for selected HFC mixtures and mixtures of the natural refrigerantsTableau 1 *Resumé des données expérimentales pour des mélanges HFC et des mélanges de frigorigènes naturels*

System/Author	No. points	Pressure range (MPa)	Temperature range (K)	Composition range (mol frac)
R32/125-VLE				
Defibaugh and Morrison ²¹	10	0.35–4.30	249–338	0.76
Fujiwara et al. ²²	8	0.69–0.82	273–273	0.06–0.90
Higashi ²³	45	0.91–2.48	283–346	0.23–0.90
Holcomb ²⁴	30	0.83–4.58	280–340	0.34–0.95
Kleemiss ²⁵	23	0.11–3.68	224–333	0.48–0.52
Nagel and Bier ²⁶	34	0.04–5.05	205–345	0.24–0.95
Oguchi et al. ²⁷	11	0.36–5.65	250–350	0.87
Piao et al. ²⁸	10	0.54–1.07	263–283	0.37–0.90*
Widiatmo et al. ²⁹	24	0.88–2.31	280–310	0.20–0.90
R32/125-P-ρ-T				
Holcomb ²⁴	45	0.90–4.61	279–341	0.24–0.96
Kiyoura et al. ³⁰	94	1.83–5.24	330–440	0.37–0.61
Kleemiss ²⁵	415	0.02–17.11	243–413	0.50–0.51
Magee ³¹	228	2.57–35.34	200–400	0.50
Oguchi et al. ²⁷	6	6.31–16.88	355–430	0.87
Piao et al. ²⁸	533	0.57–15.00	263–393	0.37–0.90
Sato et al. ³²	156	1.78–5.27	320–440	0.70–0.90
Weber and Defibaugh ³³	17	0.30–4.23	338–373	0.55
Zhang et al. ³⁴	124	0.09–4.60	300–380	0.50–0.70
R32/125-isochoric heat capacity, C_V				
Magee ³¹	111	3.43–31.93	208–345	0.50
R32/125/134a-VLE				
Higashi ³⁵	52	0.56–2.73	273–359	0.17–0.54
Holcomb ²⁴	58	0.07–3.93	221–345	0.05–0.60
Kleemiss ²⁵	44	0.07–4.20	222–353	0.14–0.66
Nagel and Bier ²⁶	29	0.03–4.77	205–362	0.19–0.43
Piao et al. ²⁸	31	0.45–2.41	270–326	0.32–0.38
Widiatmo et al. ³⁶	43	0.72–3.24	280–340	0.35–0.46
R32/125/134a-P-ρ-T				
Holcomb ²⁴	42	0.23–3.93	244–346	0.20–0.68
Kiyoura et al. ³⁰	105	1.57–5.75	315–440	0.38–0.52
Kleemiss ²⁵	369	0.03–17.11	243–413	0.33–0.35
Oguchi et al. ²⁷	12	5.19–12.39	365–430	0.38–0.47
Piao et al. ²⁸	994	0.45–15.00	263–393	0.19–0.47
Widiatmo et al. ³⁶	53	0.72–3.24	280–340	0.38–0.46
R32/134a-VLE				
Defibaugh and Morrison ²¹	25	0.26–4.47	253–358	0.50–0.55
Fujiwara et al. ²²	6	0.38–0.76	273–273	0.20–0.92
Higashi ³⁷	39	0.57–1.91	283–365	0.12–0.67
Holcomb ²⁴	48	0.38–4.56	280–340	0.16–0.78
Kleemiss ²⁵	16	0.07–3.15	223–343	0.42–0.52
Nagel and Bier ²⁶	50	0.01–5.42	203–369	0.21–0.77
Oguchi et al. ²⁷	34	0.13–1.29	238–301	0.27–0.71
Piao et al. ²⁸	10	0.24–0.93	261–283	0.33–0.89*
Widiatmo et al. ³⁸	30	0.58–3.10	280–340	0.33–0.89
R32/134a-P-ρ-T				
Holcomb ²⁴	44	0.52–4.29	279–340	0.13–0.97
Kleemiss ²⁵	390	0.02–17.11	243–413	0.50–0.56
Magee ³⁹	461	2.70–35.45	200–400	0.50–0.67
Oguchi et al. ²⁷	19	3.65–15.34	363–473	0.39
Piao et al. ²⁸	633	0.24–15.00	263–393	0.33–0.89
Sato et al. ⁴⁰	220	1.97–6.18	320–440	0.33–0.89
Weber and Defibaugh ³³	17	0.33–4.30	338–373	0.51–0.51
Widiatmo et al. ³⁶	22	1.00–3.01	280–330	0.40
R32/134a-isochoric heat capacity, C_V				
Magee ⁴¹	131	4.38–33.46	205–343	0.50
R32/134a-speed of sound, w				
Hozumi et al. ⁴²	193	0.03–0.24	303–343	0.16–0.90

Table 1 Continued

Tableau 1 Suite

System/Author	No. points	Pressure range (MPa)	Temperature range (K)	Composition range (mol frac)
R125/143a-VLE				
Higashi ³⁵	18	0.62–2.01	273–313	0.15–0.76
Holcomb ²⁴	28	0.77–2.56	280–325	0.29–0.65
Kleemiss ²⁵	16	0.09–3.30	223–338	0.46–0.50
Nagel and Bier ²⁶	19	0.03–3.69	205–343	0.49–0.50
Widiatmo et al. ⁴³	34	0.77–2.83	280–330	0.07–0.86
R125/143a- P - ρ - T				
Holcomb ²⁴	16	0.80–2.56	280–328	0.33–0.65
Kleemis ²⁵	151	1.60–17.11	243–373	0.50
Magee ⁴⁴	281	2.13–35.41	200–400	0.50
Oguchi et al. ²⁷	18	0.16–7.52	250–410	0.19
Weber and Defibaugh ³³	27	0.22–3.27	333–373	0.51
Widiatmo ⁴³	3	0.10–0.20	280–280	0.36
R125/143a-isochoric heat capacity, C_V				
Magee ⁴⁴	120	4.51–32.28	205–344	0.50
R125/143a/134a-VLE				
Bouchot and Richon ⁴⁵	18	0.30–2.88	253–333	0.36
Kleemis ²⁵	26	0.07–3.15	224–345	0.32–0.33
Nagel and Bier ²⁶	13	0.02–3.96	205–364	0.16–0.17
R125/143a/134a- P - ρ - T				
Bouchot and Richon ⁴⁵	204	0.10–18.68	253–333	0.36
Kleemis ²⁵	196	1.40–17.11	243–373	0.34
R125/134a-VLE				
Higuchi and Higashi ⁴⁶	55	0.41–2.00	283–365	0.18–0.78
Holcomb ²⁴	40	0.38–3.63	280–340	0.26–0.65
Kleemiss ²⁵	24	0.07–2.90	224–343	0.46–0.51
Nagel and Bier ²⁶	31	0.02–3.97	206–365	0.25–0.75
Widiatmo et al. ³⁶	75	0.43–2.97	280–350	0.09–0.92
R125/134a- P - ρ - T				
Holcomb ²⁴	17	0.54–2.55	280–342	0.35–0.72
Kleemiss ²⁵	407	0.02–17.11	243–413	0.50–0.51
Magee ³⁹	268	2.84–35.45	200–400	0.50
Weber and Defibaugh ³³	18	0.17–4.03	303–373	0.50
Widiatmo et al. ³⁶	110	1.00–3.02	280–350	0.09–0.92
R125/134a-isochoric heat capacity, C_V				
Magee ³⁹	94	3.81–32.11	206–345	0.50
R143a/134a-VLE				
Higashi ³⁵	10	0.52–2.82	281–340	0.35–0.65
Holcomb ²⁴	20	0.44–2.77	280–340	0.16–0.64
Kleemis ²⁵	18	0.06–3.39	223–354	0.48–0.50
Kubota and Matsumoto ⁴⁷	41	0.35–2.88	278–333	0.11–0.85
Nagel and Bier ²⁶	12	0.02–3.94	205–361	0.47–0.50
R143a/134a- P - ρ - T				
Holcomb ²⁴	13	0.52–2.82	279–340	0.35–0.65
Kleemiss ²⁵	377	0.09–17.11	243–413	0.50–0.51
R134a/152a-VLE				
Defibaugh and Morrison ²¹	13	0.10–3.43	248–368	0.78
Kleiber ⁴⁸	25	0.13–0.66	255–298	0.31–0.98
Sand et al. ⁴⁹	4	0.27–0.29	273–273	0.12–0.76
Tillner-Roth ⁵⁰	65	0.93–4.09	243–378	0.23–0.75
R134a/152a- P - ρ - T				
Dressner and Bier ⁵¹	139	0.28–56.01	333–423	0.49–0.54
Tillner-Roth ⁵⁰	1679	0.09–16.91	243–433	0.25–0.75
Weber and Defibaugh ³³	11	0.27–3.17	353–373	0.50–0.50

Table 1 Continued

Tableau 1 Suite

System/Author	No. points	Pressure range (MPa)	Temperature range (K)	Composition range (mol frac)
R134a/152a-speed of sound, w Grebekov et al. ⁵²	120	0.57–19.00	230–336	0.69
Carbon dioxide/Propane-VLE				
Acosta et al. ⁵³	289	0.06–5.86	211–350	0.08–0.44
Akers et al. ⁵⁴	15	0.10–3.50	233–273	0.05–0.82
Hamam and Lu ⁵⁵	21	0.50–2.61	244–266	0.09–0.82
Meldrum and Nielsen ⁵⁶	22	4.90–5.06	289	0.94–0.98
Nagahama et al. ⁵⁷	24	0.24–3.50	253–273	0.01–0.95
Poettman and Katz ⁵⁸	27	1.25–7.05	290–367	0.15–0.94
Reamer et al. ⁵⁹	82	0.54–6.91	278–344	0.01–0.98
Robinson and Kalra ⁶⁰	10	0.36–4.13	283	0.07–0.97
Carbon dioxide/Propane- P - ρ - T				
Mason and Eakin ⁶¹	2	0.10	289	0.50–0.50
Reamer et al. ⁵⁹	692	1.38–68.9	278–511	0.20–0.79
Carbon dioxide/Isobutane-VLE				
Besserer and Robinson ⁶²	33	0.50–7.18	311–394	0.00–0.88
Nagahama et al. ⁵⁷	20	0.01–0.24	273	0.00–1.00
Carbon dioxide/Butane-VLE				
Besserer and Robinson ⁶²	16	5.07–73.76	311	0.03–0.90
Hirata and Suda ⁶³	42	1.16–7.52	273	0.11–0.85*
Kalra et al. ⁶⁴	29	0.03–4.13	228–283	0.03–0.82
Nagahama et al. ⁵⁷	15	1.05–34.86	273	0.00–1.00
Olds et al. ⁶⁵	71	0.36–8.15	311–411	0.00–0.94
Poettman and Katz ⁵⁸	52	0.29–8.16	301–416	0.14–0.86
Carbon dioxide/Butane- P - ρ - T				
Mason and Eakin ⁶¹	4	0.10	289	0.25–0.75
Olds et al. ⁶⁵	154	1.38–68.95	311–511	0.17–0.83
Propane/isobutane-VLE				
Higashi et al. ⁶⁶	18	0.21–1.14	283–313	0.17–0.80
Hipkin ⁶⁷	86	0.12–4.17	267–394	0.00–1.00
Hirata et al. ⁶⁸	37	0.04–0.21	237–249	0.04–0.92
Hirata et al. ⁶⁹	14	1.08–2.38	340	0.05–0.99
Luo and Miller ⁷⁰	1	289	0.75	0.90
Skripka et al. ⁷¹	48	0.07–0.47	253–273	0.05–0.95
Propane/isobutane- P - ρ - T				
Hiza et al. ⁷²	8	(saturation)	105–130	0.49–0.50
Kahre ⁷³	19	0.33–1.67	289–328	0.14–0.85
Thompson and Miller ⁷⁴	4	0.14–0.14	228	0.91–0.95
Propane/isobutane/butane- P - ρ - T				
Luo and Miller ⁷⁰	2	228	0.12–0.15	0.49–0.71
Propane/butane-VLE				
Beranek and Wichterle ⁷⁵	29	0.35–3.41	303–363	0.06–0.91
Clark and Stead ⁷⁶	30	0.06–0.59	260–280	0.07–0.94
Hirata et al. ⁶⁸	35	0.02–0.21	237–249	0.05–0.95
Holcomb et al. ⁷⁷	69	0.06–3.82	237–414	0.15–0.83
Kay ⁷⁸	247	1.55–4.31	332–425	0.10–0.93
Nysewander et al. ⁷⁹	48	0.56–4.24	311–411	0.20–0.85
Skripka et al. ⁷¹	48	0.05–0.47	253–273	0.05–0.95
Propane/butane- P - ρ - T				
Acosta and Swift ⁸⁰	12	3.45–13.8	311	0.25–0.76
Hiza et al. ⁷²	8	(saturation)	110–150	0.50–0.61
Holcomb et al. ⁷⁷	129	1.81–34.93	244–400	0.61
Kahre ⁷³	20	0.26–1.63	289–328	0.15–0.84
Luo and Miller ⁷⁰	1	289	0.78	0.89
Mason and Eakin ⁶¹	2	0.10	289	0.50–0.50
Nysewander et al. ⁷⁹	45	0.56–4.24	311–411	0.20–0.85
Parrish ⁸¹	513	0.28–9.65	283–333	0.10–0.75
Thompson and Miller ⁷⁴	4	0.14–0.23	228	0.90–0.95

Table 1 ContinuedTableau 1 *Suite*

System/Author	No. points	Pressure range (MPa)	Temperature range (K)	Composition range (mol frac)
Isobutane/Butane-VLE				
Connolly ⁸²	30	8.88–33.70	344–407	0.25–0.75
Hirata and Suda ⁶³	24	0.11–0.15	273	0.09–0.93
Hirata et al. ⁸³	33	0.65–2.02	334–374	0.10–0.90
Hiza et al. ⁷²	4	(saturation)	125–140	0.47
Martinez-Ortiz and Manley ⁸⁴	30	0.14–1.04	278–344	0.25–0.75
Yokoyama and Ohe ⁸⁵	38	10.35–19.61	347–373	0.05–0.96
Isobutane/Butane- P - ρ - T				
Kahre ⁷³	16	0.20–0.71	289–328	0.21–0.80

*Listed compositions are dew point compositions.

Table 2 High-accuracy pure-fluid equations of state available for selected refrigerantsTableau 2 *Equations d'état de haute précision pour fluides purs disponibles pour les frigorigènes sélectionnés*

Fluid	Model	Source	Temperature Limits (K)	High Pressure Limit (MPa)
R11	Helmholtz	Jacobsen et al. ⁸⁷	162.68 [†] –625	30
R12	Helmholtz	Marx et al. ⁸⁸	116.10 [†] –525	200
R22	Helmholtz	Kamei et al. ⁸⁹	115.73 [†] –550	60
R32	Helmholtz	Tillner-Roth and Yokozeki ^{90*}	136.34 [†] –435	70
R113	Helmholtz	Marx et al. ⁸⁸	236.93 [†] –525	200
R123	MBWR	Younglove and McLinden ^{2*}	166 [†] –500	40
R124	Helmholtz	de Vries et al. ⁹¹	100–470	40
R125	MBWR	Outcalt and McLinden ^{92**}	172.52 [†] –500	60
R134a	Helmholtz	Tillner-Roth and Baehr ^{3*}	169.85 [†] –455	70
R143a	MBWR	Outcalt and McLinden ⁹³	161.34 [†] –500	40
R152a	MBWR	Outcalt and McLinden ⁹⁴	154.56 [†] –500	60
Propane	MBWR	Younglove and Ely ⁹⁵	85.47 [†] –600	100
Butane	MBWR	Younglove and Ely ⁹⁵	134.86 [†] –500	70
Isobutane	MBWR	Younglove and Ely ⁹⁵	113.55 [†] –600	35
Ammonia	Helmholtz	Tillner-Roth et al. ⁹⁶	195.49 [†] –700	1000
CO ₂	Helmholtz	Span and Wagner ⁹⁷	216.59 [†] –1100	800

[†]The lower temperature limit corresponds to the triple-point temperature.

*Formulation recommended as an international standard by the IEA Annex 18.

**The Annex 18-recommended formulation by Piao et al. has not yet been published.

they may not be practical in a detailed equipment simulation where properties must be evaluated many thousands of times. If only a limited range of conditions is to be considered in such a simulation, simpler models may yield good accuracy, provided that they have been optimized for that range. But the effects of using such a model should be examined. For example, see Peskin⁹⁸ for a discussion of the consequences of various property models on the computed performance of a compressor. A table look-up method, where a grid of points covering the range of interest is computed followed by interpolation among the grid points, may also be valid.

IEA Annex 18 has also considered the question of mixture models. A report by Lemmon⁹⁹ summarizes the results of a comparison of five models to the available experimental data for binary and ternary mixtures of R32, R125, and R134a. These mixtures were chosen because of their industrial importance and the avail-

ability of data. The five models came from Germany, Japan, and the United States, and represent four distinct modeling approaches. The models are a cubic equation by Zhang et al.³⁴, a modified BWR equation by Piao et al.¹⁹, an extended corresponding states model by Huber and Lemmon¹⁶, and two mixture Helmholtz models by Tillner-Roth¹⁰⁰ and Lemmon and Jacobsen¹⁷. The Annex has not endorsed any mixture model, but the report by Lemmon⁹⁹ describes the strengths and weaknesses of each.

All of the models proved very capable in representing mixture properties. Uncertainties were generally on the order of 0.5% in saturation pressures, 0.2% in density, and 1% in heat capacity. For the VLE (saturation) data, the scatter in the data masked any differences between the models. For the P - ρ - T data, each of the three binary pairs is best represented by a different equation: the Piao et al. BWR model for the R32/125 system, the Tillner-Roth Helmholtz model for the R32/134a system, and the

Table 3 Comparisons of overall average absolute deviations (%) of the models from experimental data

Tableau 3 Comparaisons des écarts absolus moyens globaux (en %) entre les modèles et les données expérimentales

Model	R32/134aP- ρ -T	R32/134aC _v	R32/125P- ρ -T	R125/134aP- ρ -T	R32/125/134aP- ρ -T
Zhang et al.	n.a.	n.a.	4.147	n.a.	n.a.
Piao et al.	0.399	0.619	0.210	0.222	0.354
Huber and Lemmon	0.463	0.711	0.689	0.236	0.439
Tillner-Roth	0.167	0.270	n.a.	n.a.	n.a.
Lemmon and Jacobsen	0.225	0.314	0.314	0.086	0.264

n.a.—model not applicable for this mixture.

Table 4 Number of coefficients in each mixture model

Tableau 4 Nombre de coefficients dans chaque modèle de mélange

Model	Type	Generalized Coefficients	Binary-Specific Coefficients
Zhang et al.	Cubic	—	18
Piao et al.	Modified BWR*	20	10
Huber and Lemmon	ECS*	—	2
Tillner-Roth	Helmholtz energy	—	7
Lemmon and Jacobsen	Helmholtz energy	10	1–4

*A separate Peng–Robinson equation of state is used to calculate vapor–liquid equilibria

Lemmon and Jacobsen Helmholtz energy model for the R125/134a system. The Lemmon and Jacobsen model best represents the R32/125/134a ternary system. But generally, all of the models have an accuracy acceptable to most engineering requirements with the exception of the Zhang et al. cubic model at pressures above 5 MPa at states away from the phase boundaries. *Table 3* gives the overall average absolute deviation of P - ρ - T and heat capacity data for each of the mixtures.

For the single set of mixture heat capacities available at the time of the comparisons, the Helmholtz energy models of Tillner-Roth and Lemmon and Jacobsen show the smallest deviations, with the Tillner-Roth model being slightly more accurate than the Lemmon and Jacobsen model. The single vapor speed-of-sound data set is well represented by the Piao et al., Tillner-Roth, and Lemmon and Jacobsen models while the ECS model of Huber and Lemmon shows small but significant (up to 0.5%) systematic deviations.

While the computational speed of the various models was not a major consideration in the Annex 18 comparisons, some general comments can be made. The Zhang et al. model, through its use of a cubic equation of state, is the fastest of the five models for computer calculations. The Huber and Lemmon ECS model requires the most time to calculate single phase properties, but VLE properties are calculated very quickly by its use of an auxiliary cubic equation. The calculation of VLE states for the Helmholtz energy models of Tillner-Roth and Lemmon and Jacobsen is slow compared to the cubic models, however, the calculated VLE states are internally consistent with the single phase properties (as is true for the Zhang et al. model).

The models differ in their generality. Two are specific to single binary pairs (Zhang et al. and Tillner-Roth). The Piao et al. model is applicable to all combinations of R32, R125, and R134a. The Huber and Lemmon, and Lemmon and Jacobsen models are more general models which have been applied to a large number of mixtures including the mixtures of R32, R125 and R134a considered in the IEA comparisons. Of course, any of the models could, in principle, be applied to additional mixtures; a rough estimate of the quantity of data required can be inferred by the number of mixture-specific parameters which must be fitted (in addition to the pure-fluid coefficients) as shown in *Table 4*. Also listed here are the number of generalized mixture coefficients, if applicable. These are coefficients which would apply to all mixtures, or at least a broad class of mixtures, and would not have to be fitted for a single given binary.

The Tillner-Roth Helmholtz energy model can represent a system with the highest accuracy using the fewest coefficients. However, it is specific to the R32/134a system and cannot be extended to ternary systems using the current functional form. The Huber and Lemmon ECS model is the most predictive of the models, requiring only two coefficients per system. However, its accuracy is not as high as the other models. The Lemmon and Jacobsen Helmholtz model is also predictive in nature, requiring only one to four fitted parameters per binary system, but with accuracies generally within experimental uncertainties. The cubic model of Zhang et al. and the modified BWR equation of Piao et al. require a large number of fitted coefficients; extension of these models to additional mixtures would require extensive data.

Conclusions

The field of refrigerant property research has seen tremendous activity in recent years. While significant progress has been made, property models for refrigerants, particularly those for mixtures, are still under development, and the coming years promise still better models. But the engineer faced today with designing a refrigeration system using one of the new refrigerants does not have the option of waiting for the 'ultimate' property model. For the pure fluids R123, R134a, R32, and R125, we recommend the use of the equations of state sanctioned by IEA Annex 18 as international standards. Models of similar form and comparable accuracy are also available for many other fluids which the Annex has not evaluated.

For the properties of mixtures, a variety of approaches are available, and for the five mixture models considered in the comparisons of IEA Annex 18 all did a commendable job. Each model has its own strengths and weaknesses. Simpler models, such as cubic equations of state, also have their place, provided they are validated against data and used within their limits of applicability. But given its combination of excellent accuracy and great generality, we recommend the Helmholtz energy mixture model of Lemmon and Jacobsen as the best available today.

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