Development of Thermodynamic Property Models for Refrigerant Mixtures

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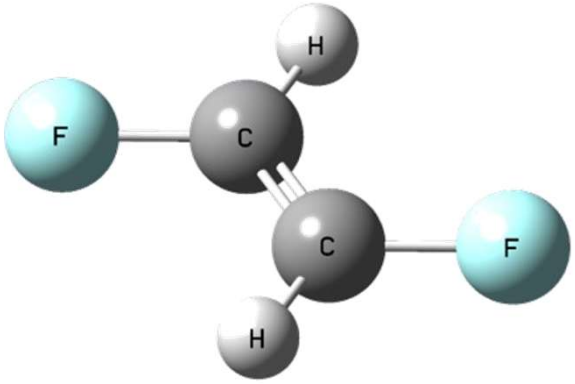
INTRODUCTION

- *trans*-1,2-Difluoroethene [R1132(E)] is a fluorinated ethene isomer, and its mixtures with R32 and/or R1234yf are one possible alternative to pure R32 for residential air conditioners. Thermodynamic property models are strongly desired for these pure fluid and mixtures.
- The first fundamental equation of state (FEQ) for R1132(E) was developed in this work based on experimental datasets, including vapor pressures, critical parameters, *pvT* relation, and sound speeds.
- In addition, tentative mixture models were fitted to R32/1132(E) and R1234yf/1132(E) mixtures, which reasonably represent *pvTx* relation and VLE behavior of these mixtures.



R1132(E)
(*trans*-1,2-difluoroethene,
CAS No. 1630-78-0)

FUNDAMENTAL EOS FOR PURE R1132(E)

Helmholtz Energy Equation of State

$$\frac{a(T,\rho)}{RT} = \alpha(\tau,\delta) = \alpha^{\circ}(\tau,\delta) + \alpha^{\mathrm{r}}(\tau,\delta)$$

dimensionless Helmholtz energy — Ideal-gas part — Residual part

Independent variables:

$\tau = T_c/T$ (reciprocal reduced temperature)

$\delta = \rho/\rho_c$ (reduced density)

Real-fluid Helmholtz energy

Ideal-gas property

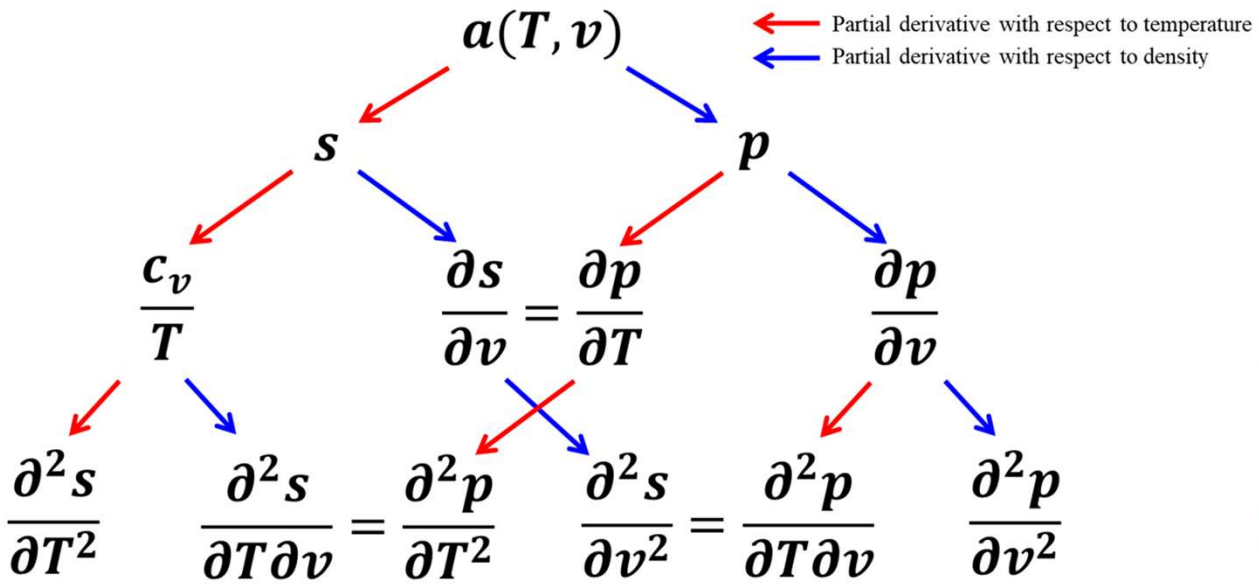
Influence of the intermolecular forces

Actually, the residual part makes a negative contribution to the real-fluid Helmholtz energy.

Ideal-gas part: Integration of an equation for the ideal-gas isobaric heat capacity (theoretical)

Residual part: Non-linear least square fitting to selected experimental data (empilical)

Why the Helmholtz energy equation is best?



$$u = a + Ts$$
$$h = a + Ts + pv$$

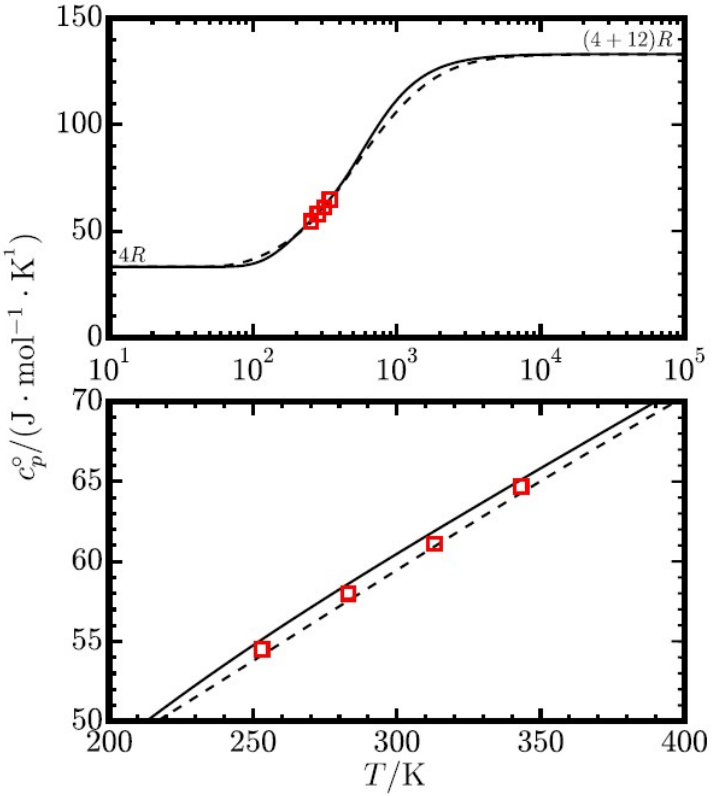
$$c_p = c_v - T\left(\frac{\partial v}{\partial p}\right)\left(\frac{\partial p}{\partial T}\right)^2$$

$$w^2 = -v^2 \frac{c_p}{c_v}\left(\frac{\partial p}{\partial v}\right)$$

Helmholtz energy equations of state with independent variables of temperature and density (or molar volume) are **one of four fundamental forms** in thermodynamics; ALL thermodynamic properties are derived only from the derivatives of the Helmholtz energy (no integration).

Formulation of the Ideal-gas part

- The ideal-gas part of the Helmholtz energy is analytically obtained from an equation for the ideal-gas isobaric heat capacity (c_p^0).
- The equation for the c_p^0 is initially formulated by fitting to rigid-rotor harmonic-oscillator (RRHO) approximation.
- The c_p^0 equation is further adjusted so that vapor-phase sound speed data are well represented by the full FEQ.
- The final c_p^0 equation represents the experimental data by Kano almost within their uncertainties.



Ideal-gas isobaric heat capacity of R1132(E): (□) Kano (unpublished data); (solid line) this work; (dashed line) Rigid-rotor harmonic-oscillator (RRHO) approximation by Gaussian 09 D.01 with B3LYP/6-31 G(d,p).

Fitting of the residual part

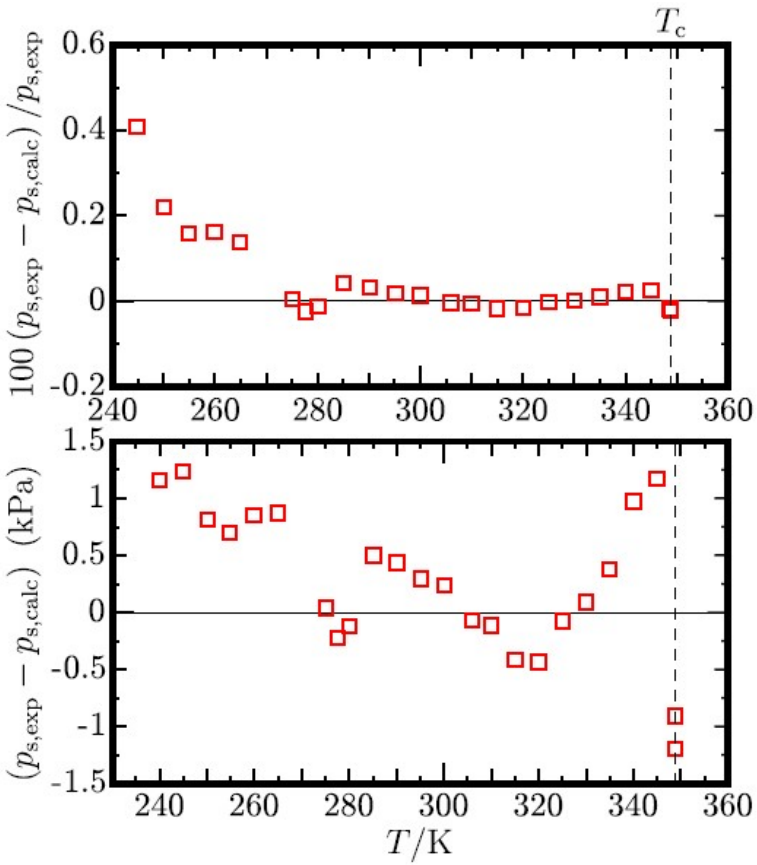
- The non-linear least square fitting originally developed by Lemmon and Jacobsen (2005) is applied to selected experimental data.
- Recent trend in the development of accurate equations of state often uses the following functional form for the residual part:

$$\alpha^r(\tau,\delta) = \underbrace{\sum N_i \tau^{t_i} \delta^{d_i}}_{\text{Polynomial terms}} + \underbrace{\sum N_i \tau^{t_i} \delta^{d_i} \exp(-\delta^{e_i})}_{\text{Exponential terms}} + \underbrace{\sum N_i \tau^{t_i} \delta^{d_i} \exp\left[-\eta_i(\delta-\varepsilon_i)^2 - \beta_i(\tau-\gamma_i)^2\right]}_{\text{Gaussian bell-shaped terms}}$$

- ✓ The density exponents d_i and e_i have to be positive integers so that α^r and all its derivatives with respect to density vanish in the limit of zero density.
- ✓ The temperature exponents t_i should be positive and can be real numbers, resulting in infinite contribution to the Helmholtz energy at zero temperature and in zero for the virial coefficients in the limit of very high temperatures.
- ✓ Various physically constraints should be applied in the fitting to obtain reasonable extrapolation behavior.

COMPARISONS TO EXPERIMENTAL DATA

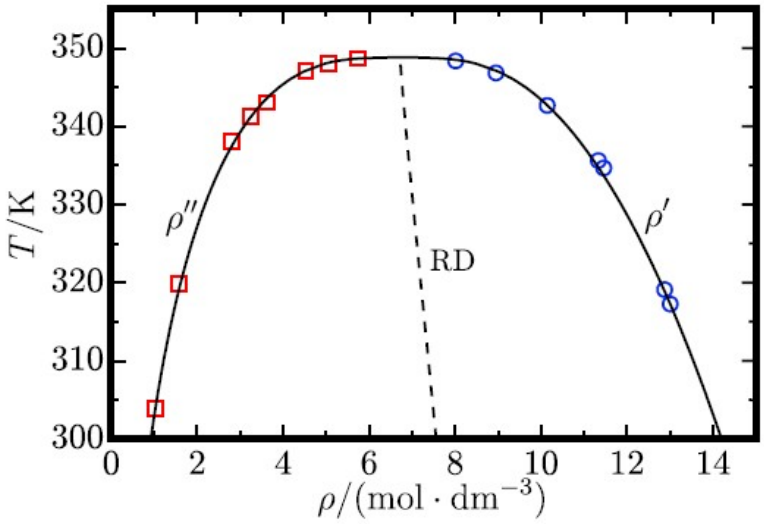
1. Vapor pressure



Relative deviations (top panel) and absolute differences (bottom panel) between experimental vapor pressures (Perera et al., 2022) and values calculated with the FEQ.

- Perera et al. (2022) measured vapor pressures of R1132(E) from 240 K to the critical temperature (348.82 K) with two different isochoric apparatuses. The expanded uncertainty (k = 2) estimated to be 1.0 kPa.
- At temperatures above 275 K, the experimental vapor pressures are represented by the FEQ within a relative deviation of 0.05 %, and the absolute differences are almost less than the experimental uncertainty.
- At lower temperatures, relative deviations tend to be greater up to 0.47 %, due to small vapor pressures, but the absolute differences are still comparable to the experimental uncertainty.
- The overall average absolute deviation (AAD) is 0.08 % and the average difference is 0.55 kPa.

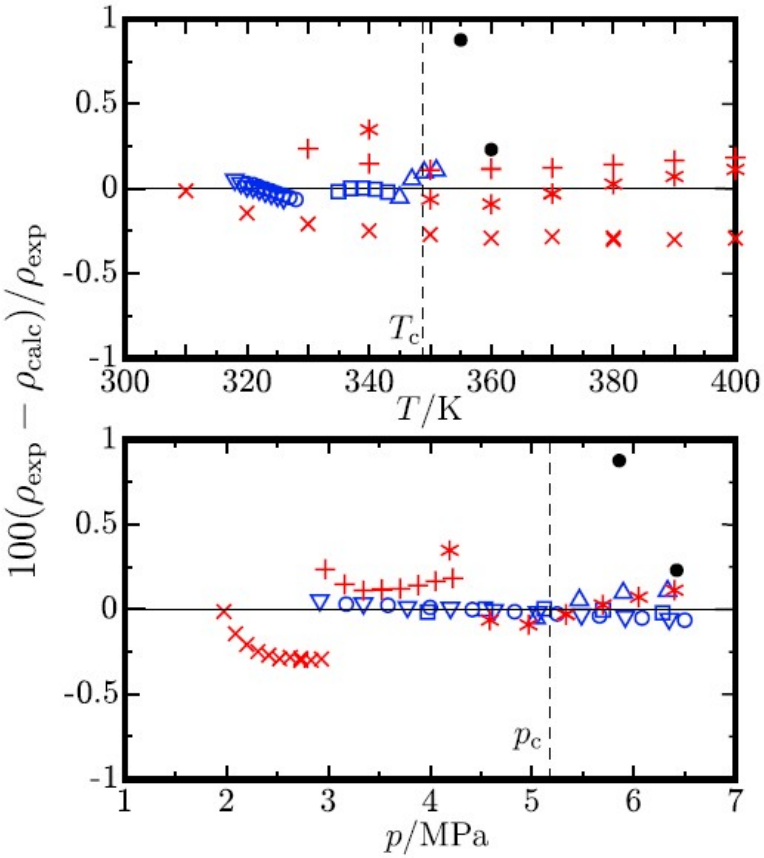
2. Saturated liquid and vapor densities



Saturation boundary calculated from the FEQ and experimental data of the saturated liquid and vapor densities (Sakoda et al., 2022): (○) saturated liquid density; (□) saturated vapor density. The dashed line (RD) indicates the rectilinear diameter.

- Sakoda et al. (2022) measured saturated liquid and vapor densities at temperatures from 304 K to 348 K with an apparatus based on the isochoric method.
- The calculated saturation boundary reasonably represents the experimental densities of Sakoda. The rectilinear diameter indicated by the dashed line (the mean value of the saturated liquid and vapor densities) is almost straight up to the critical point; this is thermodynamically correct behavior.
- The AADs are 0.83 % for the saturated liquid and 1.57 % for the saturated vapor.

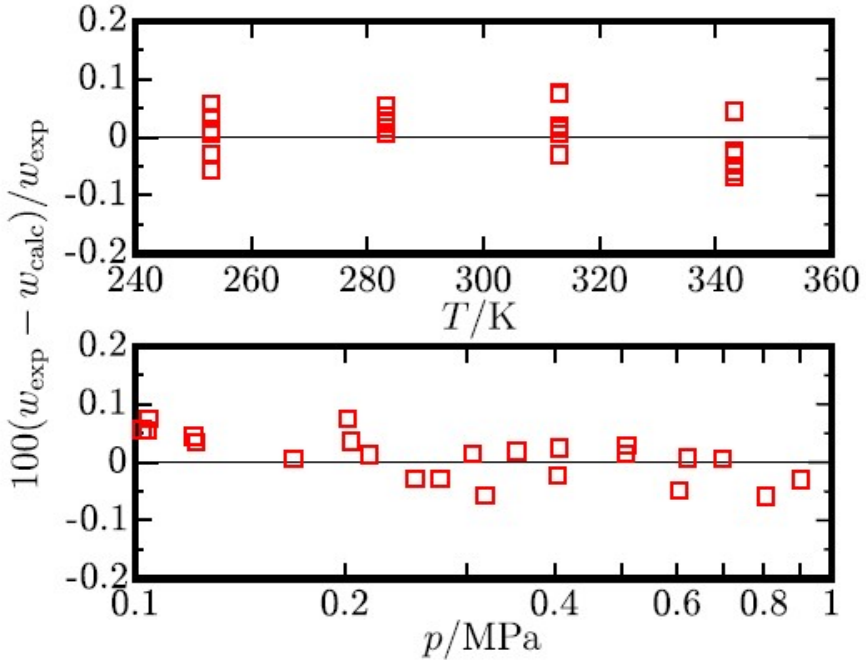
3. *pvT* relation



Relative density deviations in the experimental isochoric *pvT* data (Sakoda et al., 2022) from values calculated with the FEQ: (X) 1.0 mol · dm^{-3}; (+) 1.6 mol · dm^{-3}; (*) 2.8 mol · dm^{-3}; (●) 6.9 mol · dm^{-3}; (△) 10.1 mol · dm^{-3}; (□) 11.3 mol · dm^{-3}; (○) 12.9 mol · dm^{-3}; (▽) 13.0 mol · dm^{-3}

- Sakoda et al. (2022) obtained the *pvT* relation along eight single-phase isochores at temperatures from 318 K to 400 K and pressures up to 6.4 MPa.
- The vapor isochores (1.0 mol · dm^{-3} , 1.6 mol · dm^{-3} , and 2.8 mol · dm^{-3}) are represented almost within 0.3 %; the AAD is 0.17 %, which is similar to the experimental uncertainty (0.15 %).
- The liquid isochores (10.1 mol · dm^{-3} , 11.3 mol · dm^{-3} ,12.9 mol · dm^{-3} , and 13.0 mol · dm^{-3}) show better agreement with calculated values; the AAD is 0.03 % and all data points are represented within the uncertainty.
- Deviations in the critical isochore (6.9 mol · dm^{-3}) are larger than those in other isochores. The deviation in the data point nearest the critical point is 2.9 %.

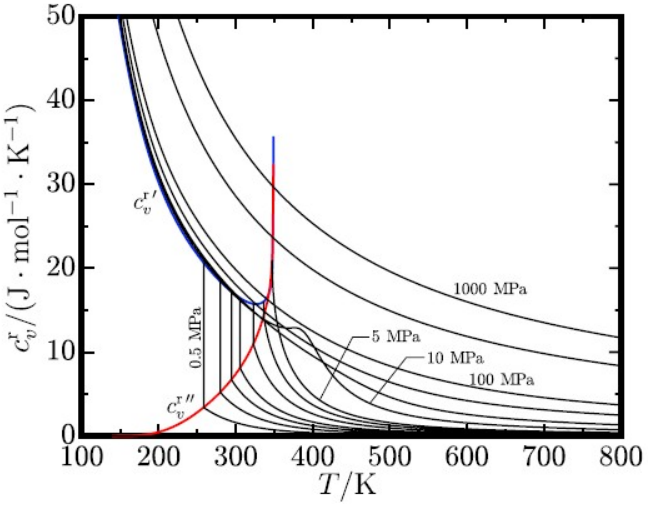
4. Sound speed



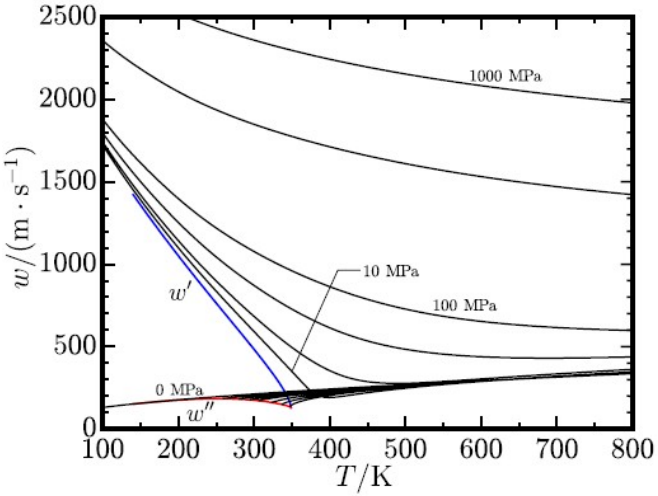
Relative deviations in experimental vapor-phase sound speed data (Kano, unpublished) from values calculated with the FEQ.

- Kano measured vapor-phase sound speeds of R-1132(E) along four isotherms at 253 K, 283 K, 313 K, and 343 K.
- The AAD in these data from values calculated with the FEQ is 0.04 % and all data points correspond to calculated values within 0.08 %. The representation of the FEQ is quite sufficient for engineering applications.

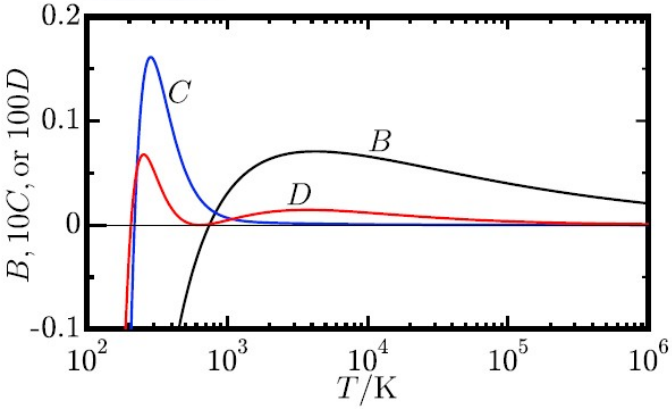
BEHAVIOR OF THE DERIVED PROPERTIES



Residual isochoric heat capacity



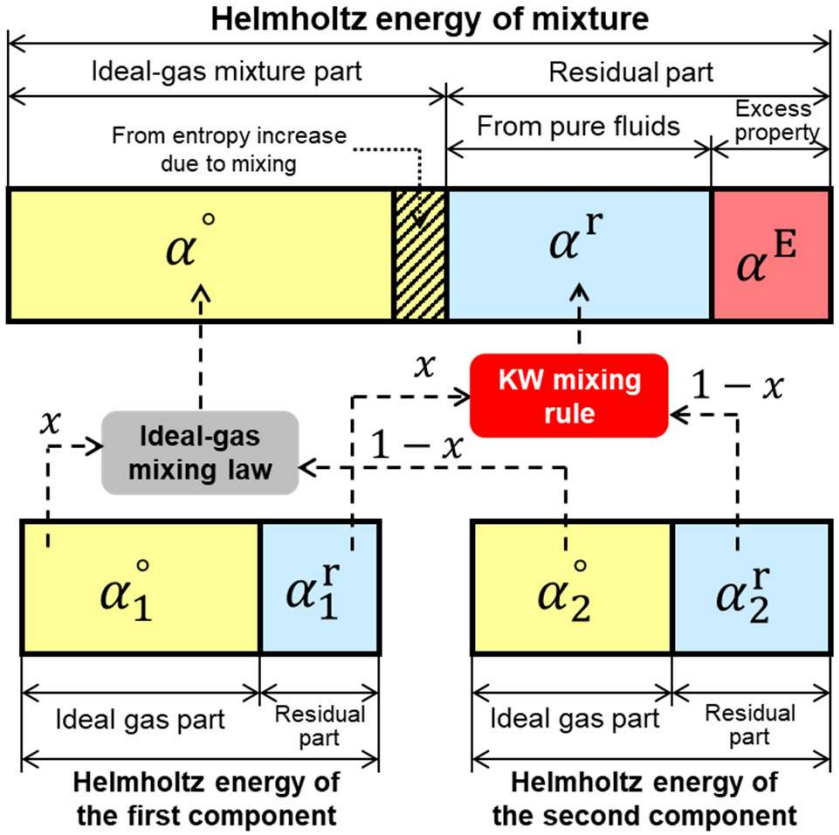
Sound speed



Second, third, and fourth virial coefficients

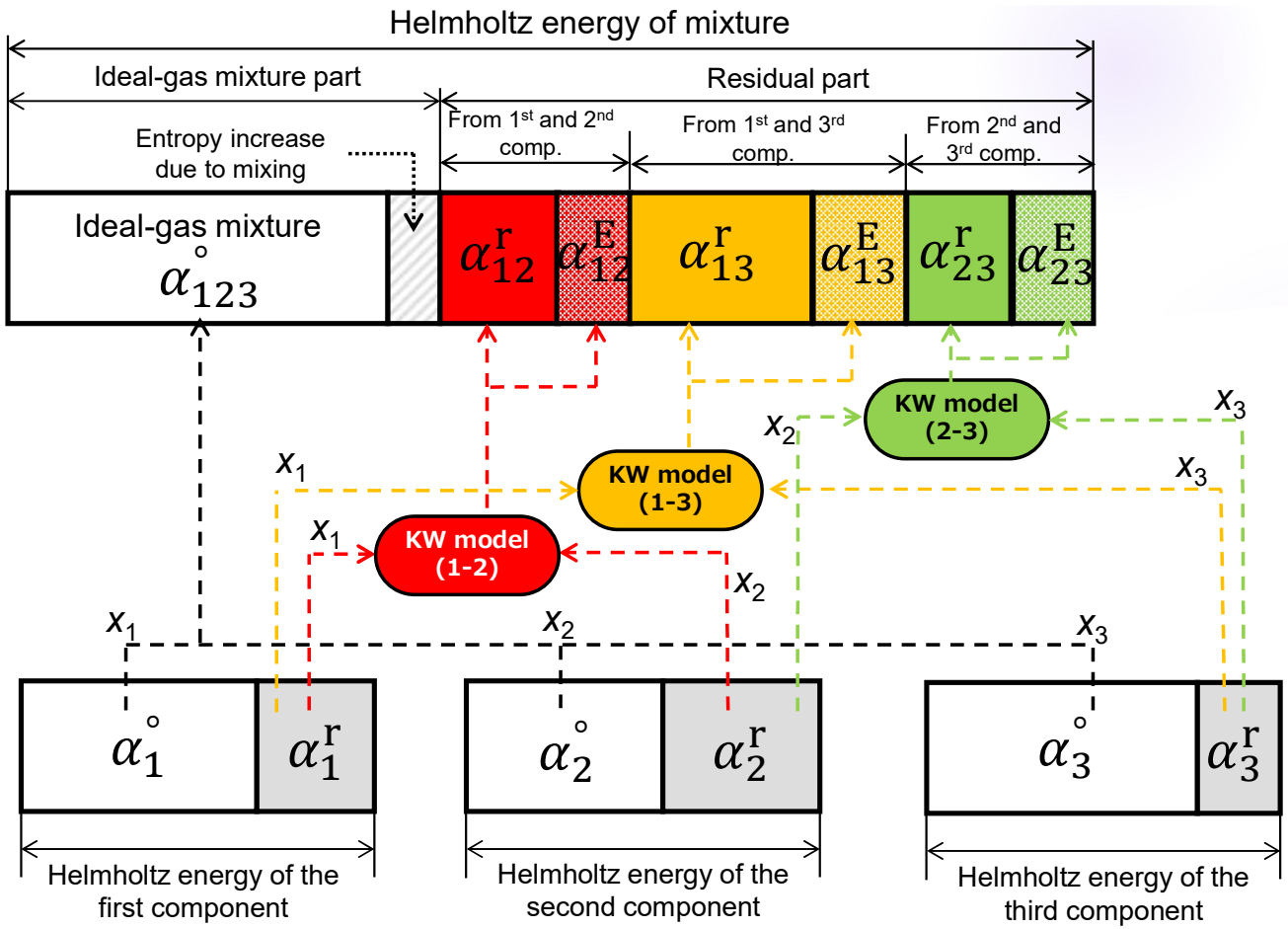
- Various thermodynamic constraints were applied to the fitting to ensure that the FEQ was well behaved near the critical point and would reliably extrapolate beyond the range of the experimental data.
- The above figures demonstrate reasonable behaviors of the FEQ not only within the range of the experimental data, but also for extrapolated states at higher temperatures and pressures, and lower temperatures.

MULTI-FLUID MIXTURE MODELS FOR R32/1132(E) AND R1234yf/1132(E) MIXTURES



Concept of the multi-fluid mixture model for binary mixtures

- In the multi-fluid mixture model, the ideal-gas mixture part of the mixture Helmholtz energy is calculated from the ideal-gas part of each pure-fluid EOS according to the ideal-gas mixing law.
- The residual part of the mixture is calculated from the residual part of each pure-fluid EOS according to a mixing rule containing empirical parameters determined by fitting to experimental data. This work adopted the **Kunz-Wagner (KW) mixing rule**.
- The excess Helmholtz energy of the mixture is calculated from a binary-specific or generalized departure function with a scaling factor determined by fitting to experimental data.



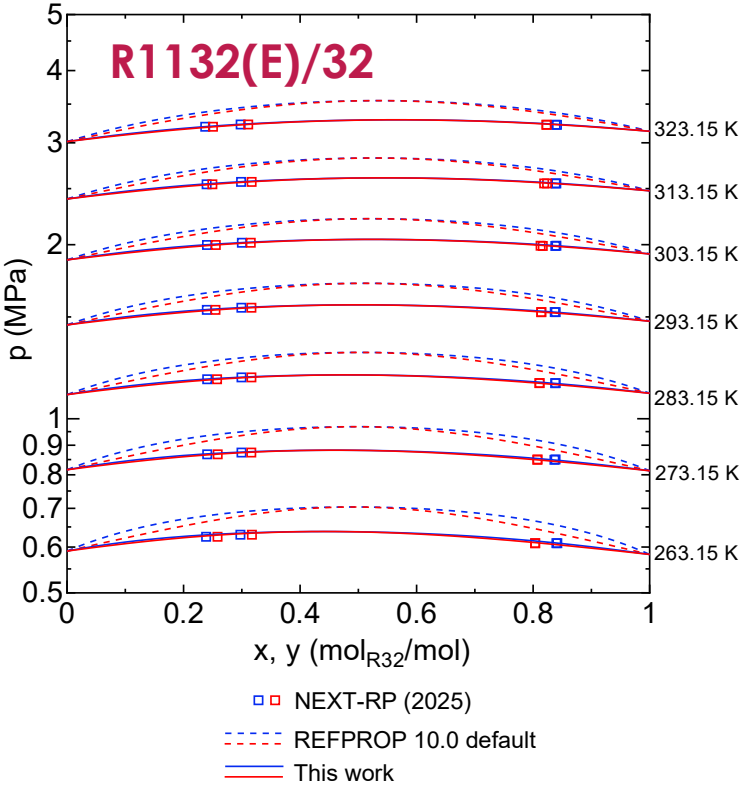
Concept of the multi-fluid mixture model for ternary mixtures

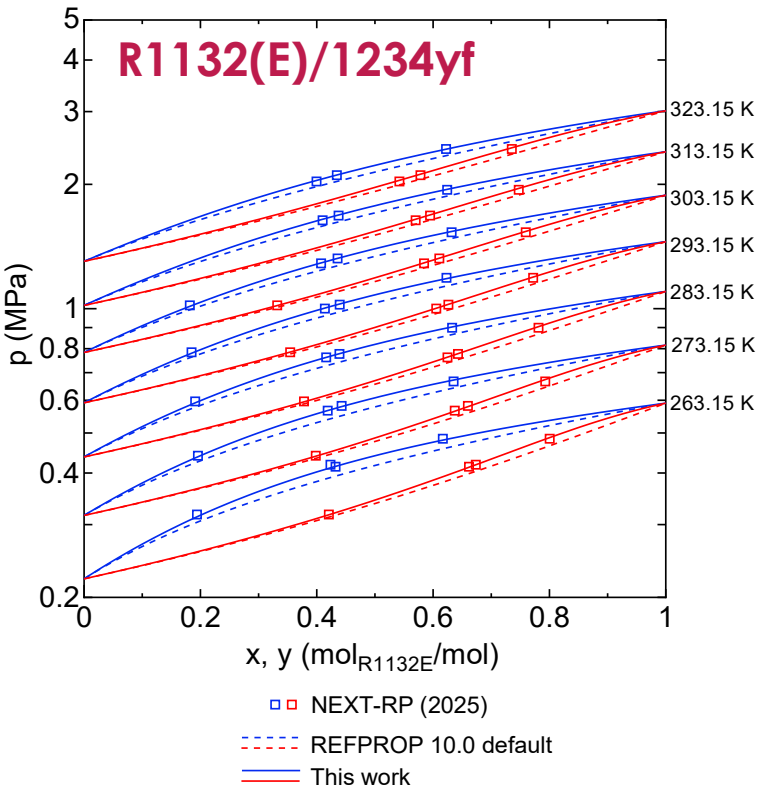
Mixing rule and departure function

- The KW mixing rule is now the most popular mixture model for refrigerant mixtures. In REFPROP 10.0, thermodynamic properties of refrigerant mixtures are calculated from this model. The KW mixing rule uses four adjustable parameters, which are normally determined by fitting to experimental data.
- For R1132(E), the FEQ developed in this work is used to calculate the ideal-gas and residual part of this refrigerant. For R32 and R1234yf, the EOS by Tillner-Roth and Yokozeki (1997) and that by Lemmon and Akasaka (2022) are used, respectively.
- This work combines the KW model with the generalized departure function for hydrocarbon mixtures, where a scaling factor is used to adjust the magnitude of the departure function to a mixture modeled. This type of mixing rule is designate the “KW0 model” in REFPROP.
- A total of five adjustable parameters (four for the KW mixing rule and one for the scaling factor of the departure function) are fitted to experimental VLE and *pVTx* data.

COMPARISONS TO EXPERIMENTAL DATA FOR THE MIXTURES R1132(E)/32 AND R1132(E)/1234yf

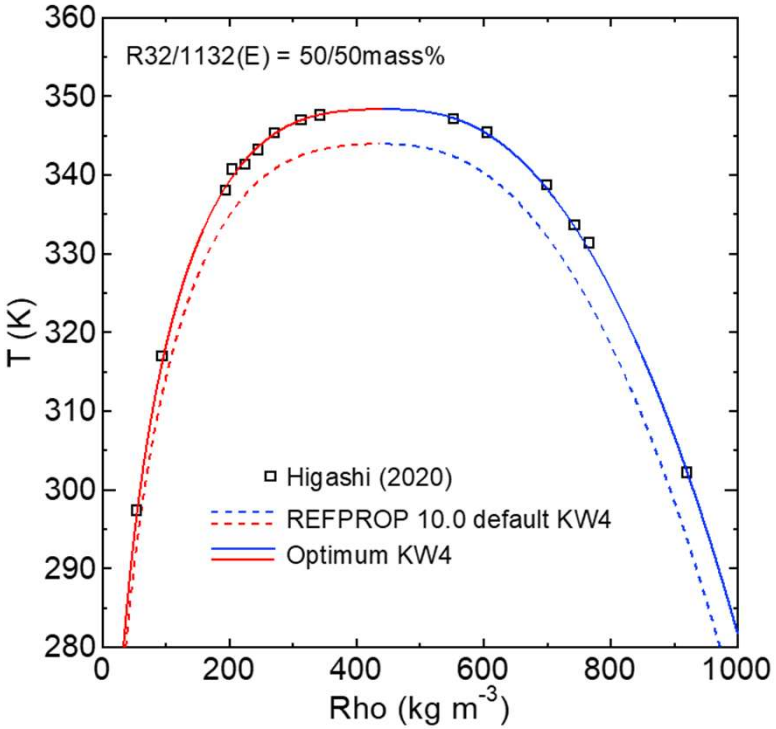
1. Vapor-liquid equilibrium



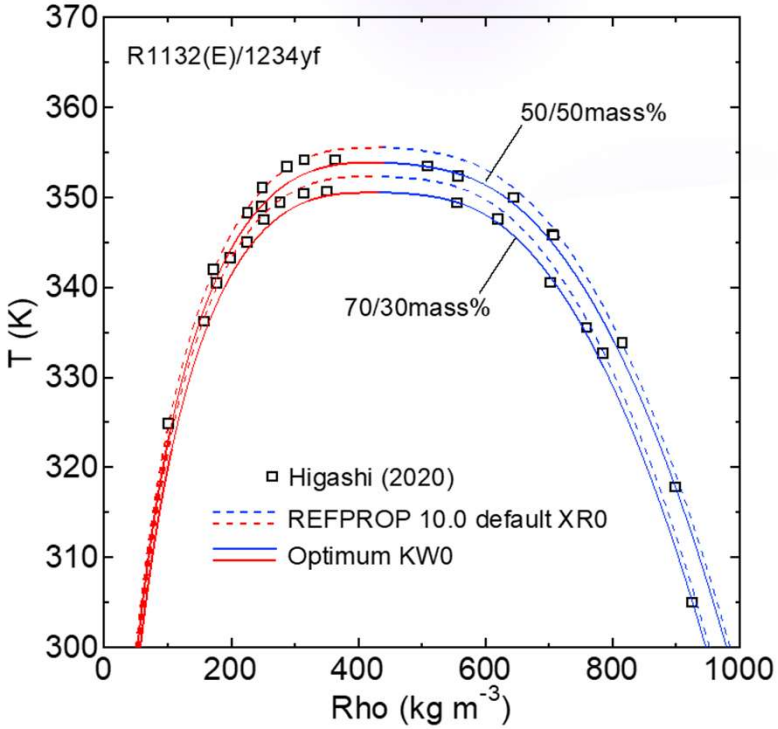


- The multi-fluid mixture models developed in this work represent more reasonably than the REFPROP 10.0 default models.
- Relative deviations in calculated bubble- and dew-point pressures from experimental values are almost within 1 %.

2. Saturation boundary near the critical point

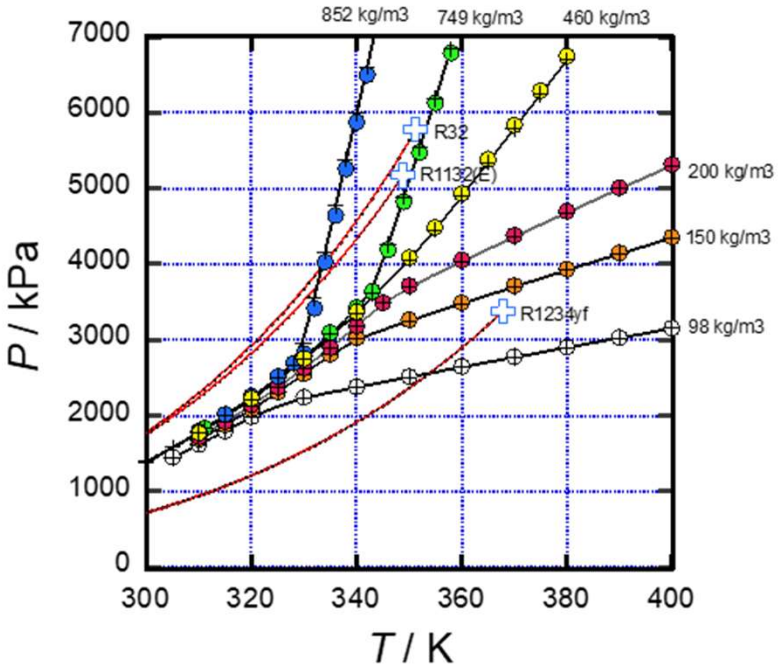


R1132(E)/32

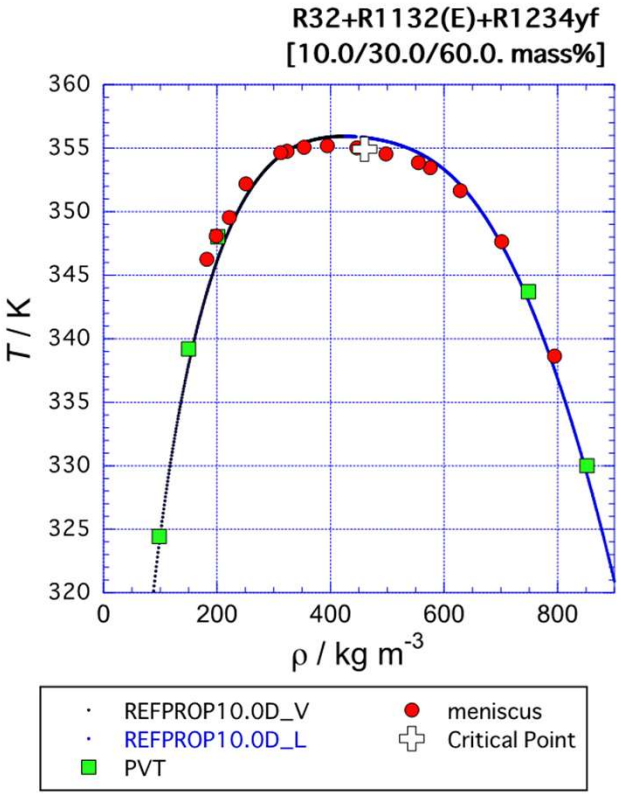


R1132(E)/1234yf

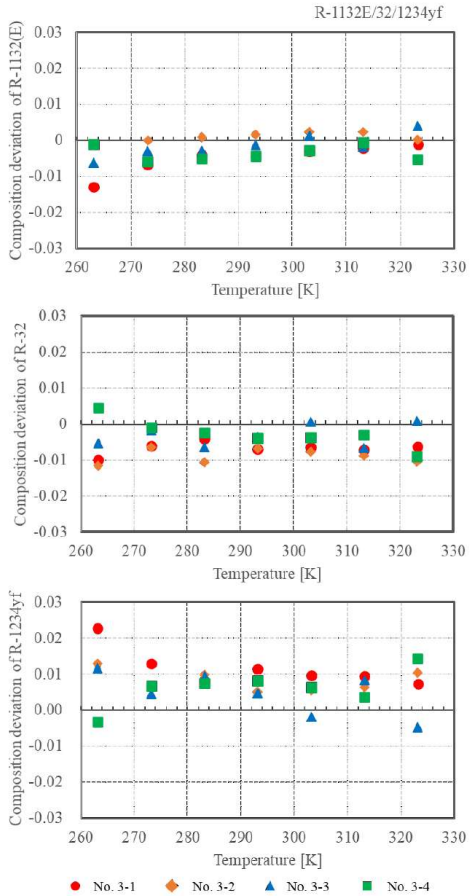
3. R1132(E)/32/1234yf ternary mixture



Experimental *PvTx* behavior and calculated values from the mixture model for the R1132E/32/1234yf ternary mixture (30.0/10.0/60.0 mass%)



Experimental saturated liquid and vapor densities and calculated saturation boundary from the mixture model for the R1132E/32/1234yf ternary mixture (30.0/10.0/60.0 mass%)



Derivations between experimental and calculated equilibrium compositions for the R1132E/32/1234yf ternary mixtures

CONCLUSIONS

- The new FEQ for R1132(E) was developed with the experimental data covering temperatures from 240 K to 400 K and pressures up to 6.5 MPa.
- Typical uncertainties in this region at the 95 % confidence interval (k = 2) are as follows:
  - ✓ liquid density: 0.1 %
  - ✓ vapor density: 0.4 %
  - ✓ vapor-phase sound speed: 0.1 %
  - ✓ vapor pressures: 0.15 %
- the new FEQ exhibits physically correct behavior over wide ranges of temperature and pressure, and it could be extrapolated to temperatures to the triple-point temperature (195.15 K) and 480 K and pressures up to 20 MPa with reasonable uncertainties.
- In addition, optimized multi-fluid mixture models were formulated for R1132(E)/32 and R1132(E)/1234yf mixtures, based on the new FEQ for R1132(E). Comparisons to experimental data show that the models successfully represent the VLE and *pVTx* data of the mixtures. It is also confirmed that these mixture models for the binary mixtures are applicable to the ternary mixture R1132(E)/32/1234yf.

See also: R. Akasaka, E. W. Lemmon, A Helmholtz Energy Equation of State for Calculations of Thermodynamic Properties of trans-1,2-Difluoroethene [R-1132(E)], *Int. J. Thermophys.*, 45(12): 174, (2024).

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Thank you.
Any questions?

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