A Thermodynamic Property Model for the R-134a/245fa Mixtures

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R-134a (1,1,1,2-tetrafluoroethane)

- Broadly used refrigerant in many applications at medium- and high-temperatures
  - Stationary commercial refrigeration
  - Chiller equipment
  - Home applications
  - Mobile air conditioners
- The GWP (1450) is far from negligible.

R-245fa (1,1,1,3,3-pentafluoropropane)

- Mainly used for high-temperature applications
  - Centrifugal chillers
  - High-temperature heat pumps
  - Organic Rankin cycles for low-temperature heat sources
- The GWP (1030) is far from negligible.

RTVF type centrifugal chiller (Ebara Refrigeration Equipment & Systems)

1. **Replacements for R-134a**
   - **R-1234yf**: lower performance, much higher production cost, slightly flammable
   - **R-1234ze(E)**: lower performance, higher production cost
   - **R-1243zf**: flammable
2. **Replacements for R-245fa**
   - **R-1234ze(Z)**: higher production cost

- Currently available replacements for R-134a and R-245fa are *still* in a development phase.
- Therefore, in at least the next decade, the refrigeration industry will use R-134a, R-245fa, and their mixtures.

Air-sourced heat pump for supplying hot water (Kobe Steel, Ltd.). This heat pump uses the R-134a/245fa mixtures as working fluid.

Objectives

The following two projects are now ongoing:

1. **Development of a new equation of state for the thermodynamic properties of pure R-245fa** (Akasaka, Zhou, and Lemmon, to be submitted to JPCRD in 2014)

2. **Development of mixture models for the R-134a/245fa mixtures** (this work) **and R-134a/1234ze(Z) mixtures** (future work)

Currently, a reliable property model is not available for the R-134a/245fa mixtures.

Outline of the model development

1. **The Kunz-Wagner (KW) mixture model** was adopted with several departure functions (12-type KW models). This approach is often used in the recent developments of accurate mixture models.
2. The most reliable pure-fluid equations of state were incorporated for calculations of the Helmholtz energies of pure fluids.
3. Adjustable parameters of the KW models were optimized by a nonlinear fitting to the following experimental data:
   - Vapor-liquid equilibirum (Bobbo et al., 2001)
   - $pvTx$ property (Higashi and Akasaka, 2014)
   - Critical temperature, critical density, and saturated liquid and vapor densities (this work)
4. The best KW model was accordingly selected that minimizes the final sum of square of relative deviations between experimental and calculated values.

Multi-fluid model for binary mixtures

$$\frac{a(T,v,x)}{RT} = \alpha = \alpha^{\mathrm{idmix}} + \alpha^{\mathrm{E}}$$

a	: Molar Helmholtz energy
R	: Universal gas constant ($= 8.3144621\ \mathrm{J\,mol^{-1}\,K^{-1}}$)
T	: Temperature
v	: Molar volume
x	: Mole fraction of the first component
α	: Reduced Helmholtz energy
α^{idmix}	: Ideal mixture contribution
α^{E}	: Contribution from mixing (Excess Helmholtz energy)

Ideal mixture contribution

$$\alpha^{\text{idmix}}(T, v, x) = x\left[\alpha_1^{\circ}(T, v) + \alpha_1^{\text{r}}(\tau, \delta) + \ln x\right] + (1 - x)\left[\alpha_2^{\circ}(T, v) + \alpha_2^{\text{r}}(\tau, \delta) + \ln(1 - x)\right]$$

$$\tau = \frac{T_{\text{red}}(x)}{T}, \quad \delta = \frac{v_{\text{red}}(x)}{v}$$

α_i° $(i = 1, 2)$: Ideal gas part of component i
α_i^{r} $(i = 1, 2)$: Residual gas part of component i
τ : Reduced mixture temperature
δ : Reduced mixture volume
T_{red} : Reducing function for temperature
v_{red} : Reducing function for volume

Table 1: Pure-fluid equations of state for the calculations of α_i° and α_i^{r}

$i = 1$ (R-134a)	Tillner-Roth and Baehr (1994)
$i = 2$ (R-245fa)	Akasaka, Zhou, and Lemmon (2014)

Reducing functions

Kunz et al. (2007) (**KW model**)

$$T_{\mathrm{red}}(x) = x^2 T_{\mathrm{c},1} + (1-x)^2 T_{\mathrm{c},2} + 2\boldsymbol{\beta_T}\,\boldsymbol{\gamma_T}\left[\frac{x(1-x)}{(\boldsymbol{\beta_T}^2 - 1)x + 1}\right] T_{\mathrm{c},12}$$

$$v_{\mathrm{red}}(x) = x^2 v_{\mathrm{c},1} + (1-x)^2 v_{\mathrm{c},2} + 2\boldsymbol{\beta_v}\,\boldsymbol{\gamma_v}\left[\frac{x(1-x)}{(\boldsymbol{\beta_v}^2 - 1)x + 1}\right] v_{\mathrm{c},12}$$

$$T_{\mathrm{c},12} = \sqrt{T_{\mathrm{c},1}\,T_{\mathrm{c},2}}$$

$$v_{\mathrm{c},12} = \frac{1}{8}\left(v_{\mathrm{c},1}^{1/3} + v_{\mathrm{c},2}^{1/3}\right)^3$$

β_T, γ_T, β_v, and γ_v: Parameters determined by the fitting to experimental data

Contribution from mixing

$$\alpha^{\mathrm{E}}(\tau, \delta, x) = x(1-x)\boldsymbol{F_{12}}\alpha^{\mathrm{r}}_{12}(\tau, \delta)$$

α^{r}_{12} : Departure function
F_{12} : Scaling factor

- Several departure functions have so far been proposed for binary mixtures including hydrocarbons, noble gases, and refrigerants.
- The scaling factor F_{12} is used to adjust the magnitude of α^{r}_{12} for a mixture of interest.

$$\boxed{\text{Multi-fluid model}} = \boxed{\text{Reducing functions}} + \boxed{\text{Departure function}}$$

A multi-fluid model is combination of departure functions for temperature and volume and a departure function representing the contribution from mixing.

Table 2: 12-type KW models

Designation	Reducing functions	Departure function
KWG	KW	generalized for binary pairs in methane, ethane, propane, n-butane, isobutane, ethylene, nitrogen, argon, oxygen, and carbon dioxide
KWR	KW	specified for R-32 + R-125 mixtures
KWS	KW	specified for R-32 + R-134a mixtures
KWT	KW	generalized for R-125 + R-134a, R-125 + R-143a, R-134a + R-143a, and R-134a + R-152a mixtures
KW0	KW	generalized for methane + n-butane, methane + isobutane, ethane + propane, ethane + n-butane, ethane + isobutane, propane + n-butane, propane + isobutane, and n-butane + isobutane mixtures
KW1	KW	specified for methane + ethane mixtures
KW2	KW	specified for methane + propane mixtures
KW3	KW	specified for methane + nitrogen mixtures
KW4	KW	specified for methane + carbon dioxide mixtures
KW5	KW	specified for nitrogen + carbon dioxide mixtures
KW6	KW	specified for nitrogen + ethane mixtures
KW7	KW	specified for methane + hydrogen mixtures

Nonlinear least square fitting of the five adjustable parameters

- Five adjustable parameters: $\boldsymbol{\beta_T}$, $\boldsymbol{\gamma_T}$, $\boldsymbol{\beta_v}$, $\boldsymbol{\gamma_v}$, and $\boldsymbol{F_{12}}$
- Modified Levenberg-Marquardt algorithm
- Objective function

$$S = \frac{1}{n_{p_\mathrm{b}}} \sum W_{p_\mathrm{b}} X_{p_\mathrm{b}}^2 + \frac{1}{n_{p_\mathrm{d}}} \sum W_{p_\mathrm{d}} X_{p_\mathrm{d}}^2 + \frac{1}{n_\rho} \sum W_\rho X_\rho^2 + \frac{1}{n_{T_\mathrm{c}}} \sum W_{T_\mathrm{c}} X_{T_\mathrm{c}}^2 + \frac{1}{n_{v_\mathrm{c}}} \sum W_{v_\mathrm{c}} X_{v_\mathrm{c}}^2$$

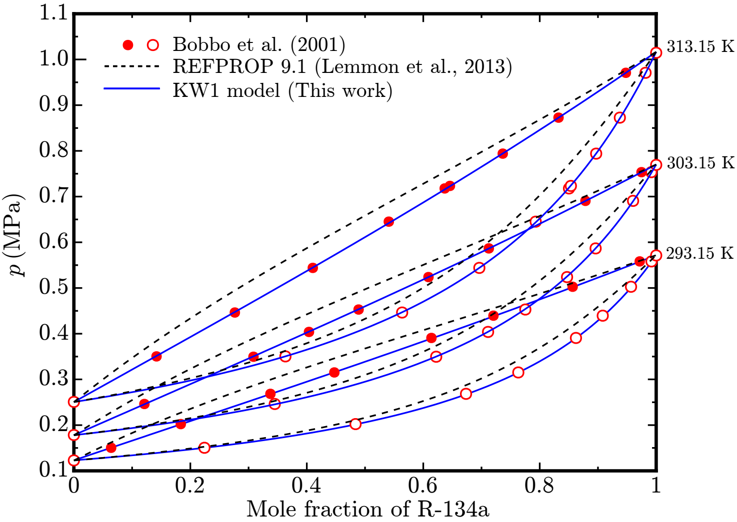
X : Relative deviation, e.g. $X_{p_\mathrm{b}} = (p_{\mathrm{b,exp}} - p_{\mathrm{b,cal}})/p_{\mathrm{b,cal}}$
W : Weighting factor
n : Number of data points

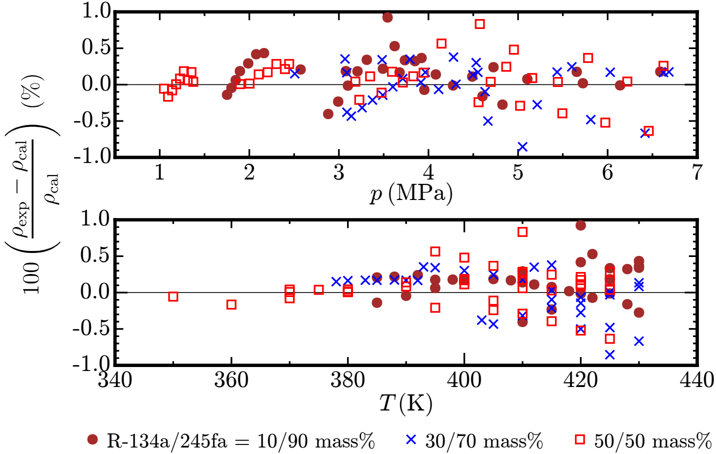
Optimum values of the adjustable parameters

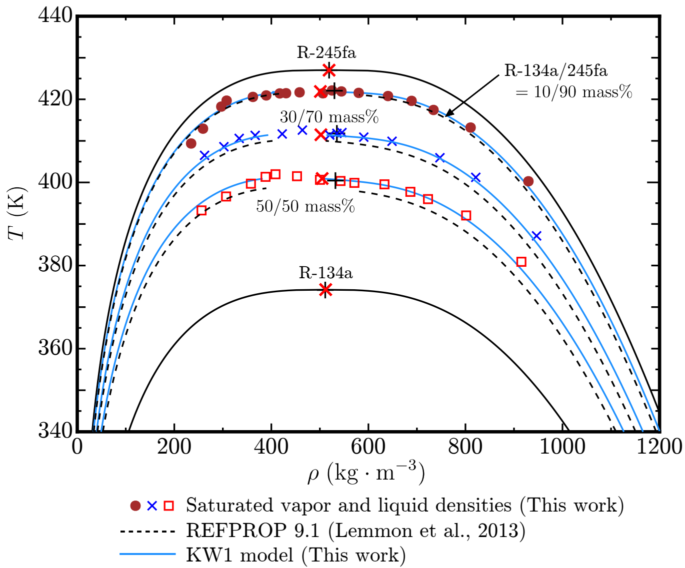
Table 3: Optimum parameters and final sum of square

Mixture model	β_T	γ_T	β_v	γ_v	F_{12}	$S_{\text{final}} \times 10^3$
KWG	1.	1.00372	0.992392	0.998056	0.145638	0.1136
KWR	1.	1.01541	0.992526	1.00950	0.185932	0.4036
KWS	1.	1.01264	0.993027	1.01662	0.539071	0.5048
KWT	1.	1.00717	0.992132	1.00391	0.909890	0.2710
KW0	1.	1.00608	0.993058	1.00117	0.0529635	0.1222
KW1	**1.**	**1.00643**	**0.992025**	**1.**	**0.107754**	**0.1128**
KW2	1.	1.00592	0.993705	1.00213	0.0500026	0.1394
KW3	0.999303	1.00604	0.993438	0.999266	0.120055	0.2690
KW4	0.999366	1.00774	0.992810	0.995019	0.123985	0.2695
KW5	1.	1.00714	0.992583	0.997638	0.0561002	0.1470
KW6	1.	1.00682	0.992581	0.997262	0.057564	0.1379
KW7	1.	0.998221	0.994407	1.01430	0.116853	0.3022

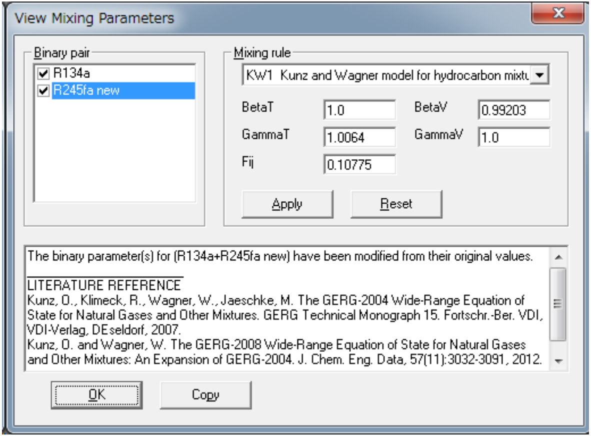
- The KW1 model is the best in 12 models for the R-134a/245fa mixtures.


Bobbo et al. (2001)
REFPROP 9.1 (Lemmon et al., 2013)
KW1 model (This work)
313.15 K
303.15 K
293.15 K
p (MPa)
Mole fraction of R-134a
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.2
0.4
0.6
0.8
1


$100\left(\frac{\rho_{exp}-\rho_{cal}}{\rho_{cal}}\right)$ (%)
1.0
0.5
0.0
-0.5
-1.0
1
2
3
4
5
6
7
p (MPa)
340
360
380
400
420
440
T (K)
R-134a/245fa = 10/90 mass%
30/70 mass%
50/50 mass%


440
420
400
380
360
340
0
200
400
600
800
1000
1200
T (K)
ρ (kg · m−3)
R-245fa
R-134a/245fa
= 10/90 mass%
30/70 mass%
50/50 mass%
R-134a
Saturated vapor and liquid densities (This work)
REFPROP 9.1 (Lemmon et al., 2013)
KW1 model (This work)

- Applying the multi-fluid model, this work successfully modeled the thermodynamic properties of the R-134a/245fa mixtures.
- The estimated uncertainties in calculated properties from the model are
  - **±0.20 %** for the bubble and dew point pressures
  - **±0.24 %** for the liquid and vapor densities
- The critical parameters of the mixtures are also properly represented with the model. The calculated critical temperatures correspond to experimental values within **±0.5 K**.
- The model allows reliable analysis of refrigeration systems or heat pumps using the mixtures.



The parameters determined in this work can be applied to REFPROP.

Thank you.

Any questions?

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