A Helmholtz energy equation of state for calculating the thermodynamic properties of fluid mixtures

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Abstract

- New Approach
  - based on highly accurate EOS for the pure components combined at the reduced T, ρ of the mixture
  - reducing parameters for the T,ρ : composition
- For simple mixtures
  - with relatively simple functions
    - ➔very accurate representation
- For nonideal mixtures
  - modified reducing func.(T, ρ)+departure func.
    - ➔0.1% in density, 1% in C_v, 1% in bubble point pressure

Abstract

- Two applications of mixture model concepts
  - developed independently in USA and Germany over the same time period
  - including the development of individual equation for each binary system
    - ➔generalization of the model for a wide variety of mixtures
  - Similarities and differences

Introduction

- Dimensionless Helmholtz energy, $\alpha = A/RT$
  - Thermodynamic properties of pure fluids with high accuracy over a wide range of T, P
  - All thermodynamic properties from a single mathematical relation
  - A large number of adjustable coeff. (up to 58 terms reported)
  - Reference equation for the calculation of property tables and chart
    - ➔accuracy : restricted only by the accuracy of available measurements

Introduction

- Due to the complexity
  - Equation with many coefficients
    - ➔applied only to pure fluids
  - High-accuracy EOS
    - ➔developed for only about 30 pure substances

- Only a few attempts to describe mixture properties using multiparameter EOS

Introduction

- Plocker et al. (1978)
  - one-fluid theory applied to modified Benedict-Webb-Rubin(mBWR) EOS
  - with a mixing rule for the pseudo-critical temperature
  - VLE and Enthalpies at high pressures
- Platzer and Maurer (1993)
  - generalized the 20-term Bender equation
  - prediction for multicomponents mixture properties
- Huber and Ely (1994)
  - extended corresponding states model based on mBWR EOS

Introduction

- Mixture model (pure → mixture)
  - ▶ based on high-accuracy pure fluid EOS for the pure components
  - ▶ pressure-explicit EOS
    - ➔ simple integration of pressure
      - ✱ generally explicit in Helmholtz energy
        - ⏩ adopted for the mixture
  - ▶ combination rules for the Helmholtz energy function of mixture components (not mixing rules)
    - ➔ not required a fixed structure of the pure fluid equation
  - ▶ single mathematical expression

Introduction

- General form of Helmholtz energy model
  - independently developed by both authors during overlapping periods of time
- Tillner-Roth (1993)
  - focused on developing an accurate formulation for individual binary mixtures for a large amount of accurate experimental data
- Lemmon (1996)
  - focused on developing a generalized model capable of accurate property calculation for a large number of fluid mixtures

Introduction

- Purpose
  - additional detail and background for the models
    - ➔especially ideal mixture
  - difference between the models

Helmholtz energy

- EOS for the pure fluids
  - ▶ ideal part + residual part

$$\frac{A}{RT}=\alpha(\tau,\delta)=\alpha^{0}(\tau,\delta)+\alpha^{\mathrm{r}}(\tau,\delta)$$

$$\alpha^{0}(\tau,\delta)=\ln\delta+c_1\ln\tau+\sum_{k=2}^{k1}c_k\tau^{m_k}+\sum_{k=k1+1}^{k2}c_k\ln\left[1-\exp(-a_k\tau)\right]$$

$$\alpha^{\mathrm{r}}(\tau,\delta)=\sum_{k=k2+1}^{k3}c_k\delta^{n_k}\tau^{m_k}+\sum_{k=k3+1}^{k4}c_k\delta^{n_k}\tau^{m_k}\exp\left(-\delta^{e_k}\right)$$

$$\tau=\frac{T_n}{T},\ \delta=\frac{\rho}{\rho_n}=\frac{V_n}{V}$$

  - ▶ reducing parameter T_{n}, V_{n} : critical properties

Helmholtz energy

- Transforming into the Helmholtz energy form by integrating the relation

$$p = \rho R T\left[1 + \delta\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \delta}\right)_{\tau}\right]$$

Mixture Model

- α of mixture : composition dependence

$$\alpha = \alpha^0 + \alpha^r$$

- Ideal gas mixture : analytically from functions for the ideal gas properties of the pure fluids

$$\alpha^0 = \alpha^0(T, V, \mathbf{x}) = \sum_{i=1}^{l} x_i \alpha_i^0(T, V) + \sum_{i=1}^{l} x_i \ln x_i$$

  - ▶ consistent with ideal parts of the pure fluid equation with independent reduced variable τ, δ

Mixture Model

- Residual Helmholtz energy

$$\alpha^{\mathrm{r}}(\tau,\delta,\mathbf{x}) = \sum_{i=1}^{l} x_i \alpha_i^r(\tau,\delta) + \Delta\alpha^{\mathrm{r}}(\tau,\delta,\mathbf{x})$$

  - linear combination of the pure fluid residual energy
  - departure function, $\Delta\alpha^{\mathrm{r}}$
    - ➔interaction of different species in the mixture
  - Corresponding states principle
    - ➔shape factors : ratios of the critical properties

$$T_r = T \cdot h = T\frac{T_{n,r}}{T_n}, \quad \tau_r = \frac{T_{n,r}}{T_r} = \frac{T_n}{T} = \tau$$

Mixture Model

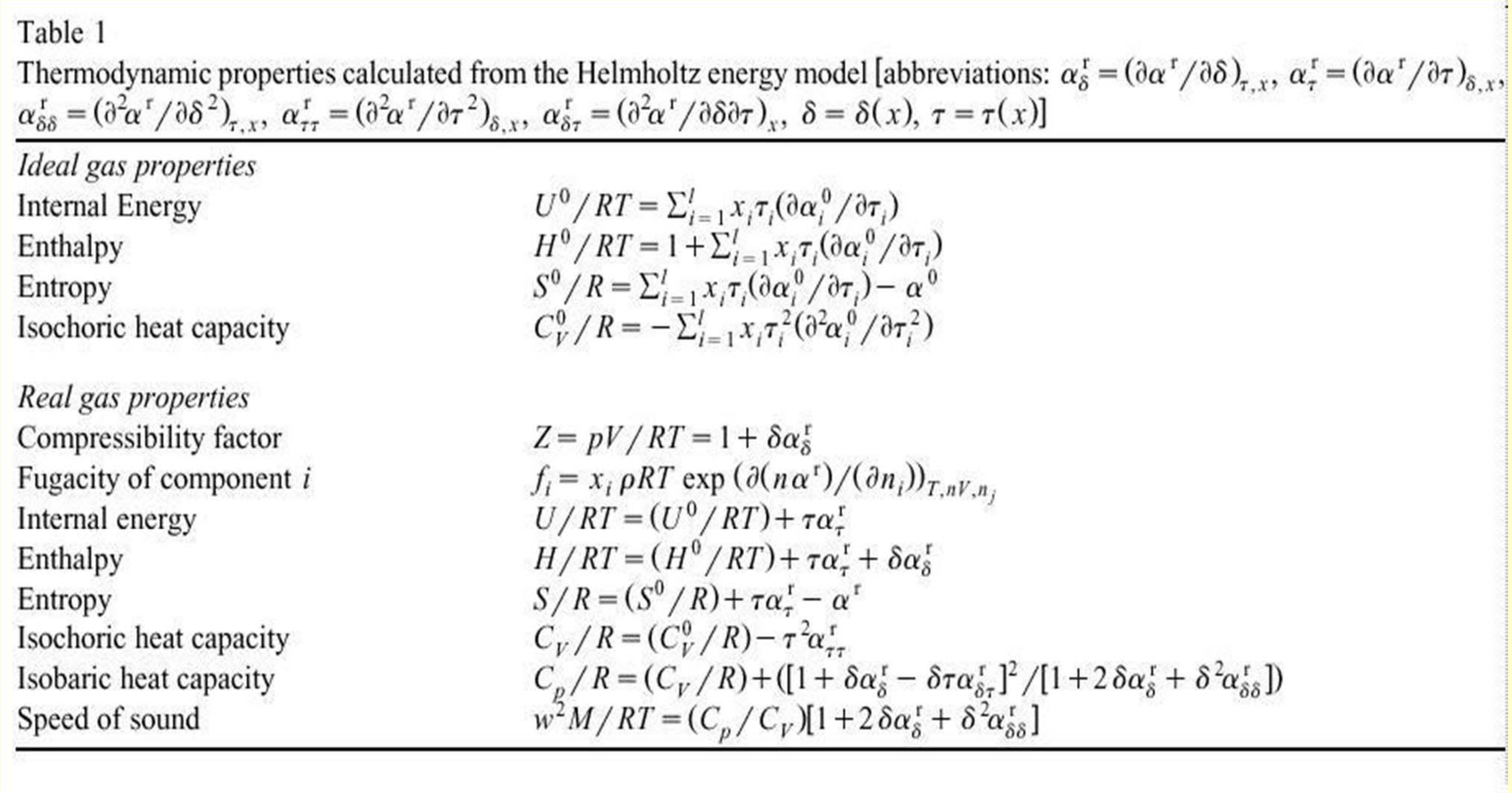

Table 1

Thermodynamic properties calculated from the Helmholtz energy model [abbreviations: $\alpha^{\mathrm{r}}_{\delta} = (\partial\alpha^{\mathrm{r}}/\partial\delta)_{\tau,x}$, $\alpha^{\mathrm{r}}_{\tau} = (\partial\alpha^{\mathrm{r}}/\partial\tau)_{\delta,x}$, $\alpha^{\mathrm{r}}_{\delta\delta} = (\partial^2\alpha^{\mathrm{r}}/\partial\delta^2)_{\tau,x}$, $\alpha^{\mathrm{r}}_{\tau\tau} = (\partial^2\alpha^{\mathrm{r}}/\partial\tau^2)_{\delta,x}$, $\alpha^{\mathrm{r}}_{\delta\tau} = (\partial^2\alpha^{\mathrm{r}}/\partial\delta\partial\tau)_{x}$, $\delta = \delta(x)$, $\tau = \tau(x)$]

Ideal gas properties	
Internal Energy	$U^0/RT = \Sigma^{l}_{i=1} x_i \tau_i (\partial\alpha^0_i/\partial\tau_i)$
Enthalpy	$H^0/RT = 1 + \Sigma^{l}_{i=1} x_i \tau_i (\partial\alpha^0_i/\partial\tau_i)$
Entropy	$S^0/R = \Sigma^{l}_{i=1} x_i \tau_i (\partial\alpha^0_i/\partial\tau_i) - \alpha^0$
Isochoric heat capacity	$C^0_V/R = -\Sigma^{l}_{i=1} x_i \tau_i^2 (\partial^2\alpha^0_i/\partial\tau_i^2)$
Real gas properties	
Compressibility factor	$Z = pV/RT = 1 + \delta\alpha^{\mathrm{r}}_{\delta}$
Fugacity of component i	$f_i = x_i\,\rho RT\,\exp\,(\partial(n\alpha^{\mathrm{r}})/(\partial n_i))_{T,nV,n_j}$
Internal energy	$U/RT = (U^0/RT) + \tau\alpha^{\mathrm{r}}_{\tau}$
Enthalpy	$H/RT = (H^0/RT) + \tau\alpha^{\mathrm{r}}_{\tau} + \delta\alpha^{\mathrm{r}}_{\delta}$
Entropy	$S/R = (S^0/R) + \tau\alpha^{\mathrm{r}}_{\tau} - \alpha^{\mathrm{r}}$
Isochoric heat capacity	$C_V/R = (C^0_V/R) - \tau^2\alpha^{\mathrm{r}}_{\tau\tau}$
Isobaric heat capacity	$C_p/R = (C_V/R) + ([1 + \delta\alpha^{\mathrm{r}}_{\delta} - \delta\tau\alpha^{\mathrm{r}}_{\delta\tau}]^2/[1 + 2\delta\alpha^{\mathrm{r}}_{\delta} + \delta^2\alpha^{\mathrm{r}}_{\delta\delta}])$
Speed of sound	$w^2 M/RT = (C_p/C_V)[1 + 2\delta\alpha^{\mathrm{r}}_{\delta} + \delta^2\alpha^{\mathrm{r}}_{\delta\delta}]$

Mixture Model

- Reducing parameter of the pure fluid equation
  $\neq$ reducing functions of the mixture
  - ▶ *pseudo-critical* parameter τ, δ
    - ➔composition dependence

$$\tau(\mathbf{x}) = \frac{T_n(\mathbf{x})}{T}, \delta(\mathbf{x}) = \frac{V_n(\mathbf{x})}{V}$$

➔as x_i approaches 1

$$T_n(\mathbf{x}) \to T_{n,i}, V_n(\mathbf{x}) \to V_{n,i}$$

or

$$\tau(\mathbf{x}) \to \tau_i, \delta(\mathbf{x}) \to \delta_i$$

Linear mixture model

- Linear mixture model
  - ▶ linear combinations of the pure fluid parameters

$$T_n(\mathbf{x}) = \sum_{i=1}^{l} x_i T_{n,i}, \quad V_n(\mathbf{x}) = \sum_{i=1}^{l} x_i V_{n,i}$$

  - ▶ departure function $\Delta\alpha^{\mathrm{r}}$ omitted
    - ➔no adjustable parameters

Linear mixture model : Application

- 1,1,1,2-tetrafluoroethane(R-134a) +difluoromethane(R-32)
    - ➔close behavior of an ideal solution
  - ▶ VLE : excellent results (Fig.1a)
  - ▶ Density in subcritical range (Fig.2a)
    - ➔vapor, liquid density : good agreement
  - ▶ Density in supercritical range (Fig.2b)
    - ➔larger deviation
  - ▶ Isochoric heat capacity
    - ➔±1%(about the experimental uncertainty)

Linear mixture model : Application

- water+ammonia
  - ➔ mixture of polar components showing large mixing effects, wide two-phase region
- ▶ VLE (Fig.1b)
  - ➔dew curve : well
    - ✱high conc. in the vapor phase→ideal at lower pressures
  - ➔bubble curve : large deviation
- ▶ Density (Fig.2c)
  - ➔-1% ~ +3% deviation
- ▶ Excess enthalpy (Fig.3c)
  - ➔poor representation : related to VLE

Linear mixture model : Application

- ethane+carbon dioxide
        - ➔azeotropic behavior
    - ▶ VLE (Fig.1c)
        - ➔incorrect prediction
    - ▶ Isochoric heat capacity (Fig.3b)
        - ➔less accurate
        - ➔>2% deviation outside of the critical region

Linear mixture model : Application

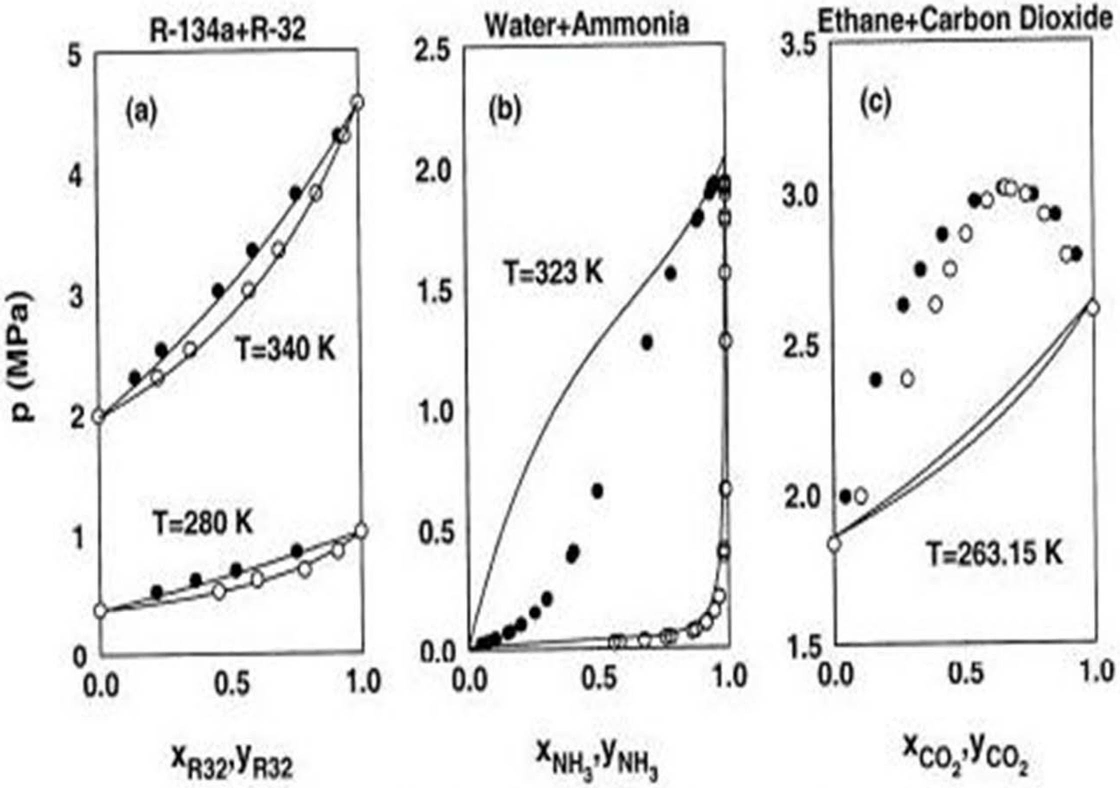

Fig. 1. Experimental and calculated VLE state points from the linear mixture model. (a) R-134a + R-32: ○, ● Holcomb et al. [6]. (b) Water + ammonia: ○, ● Smolen et al. [26]. (c) Ethane + carbon dioxide: ○, ● Fredenslund and Mollerup [3].

Linear mixture model : Application

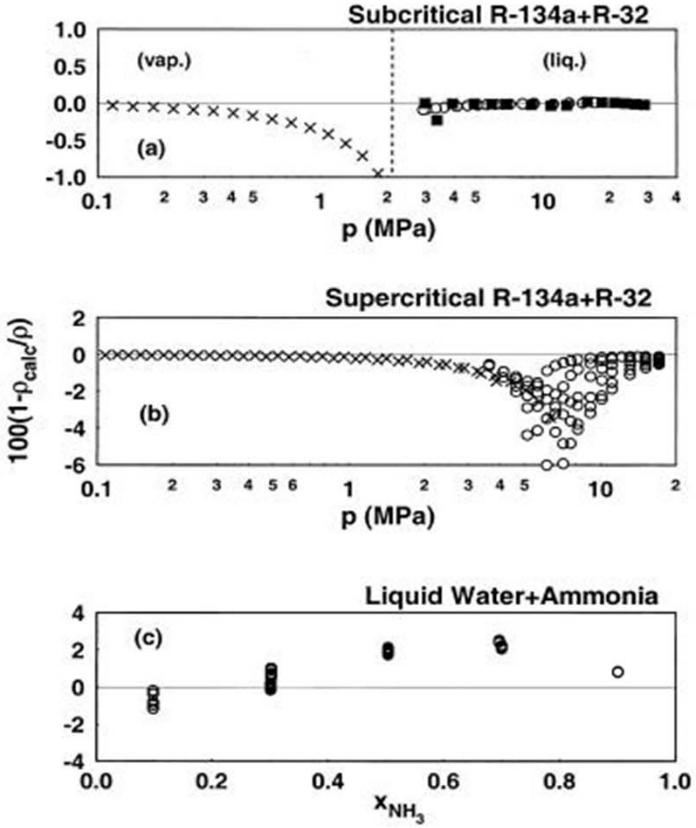

Fig. 2. Density deviations between experimental data and densities calculated from the linear mixture model. (a) Subcritical R-134a + R-32 ($T = 333.15$ K, $x \approx 0.5$): ×, ○ Kleemiss [9]; ■ Magee and Haynes [15]. (b) Supercritical R-134a + R-32 ($363 < T$ (K) < 413, $x \approx 0.5$): ×, ○ Kleemiss [9]. (c) Liquid water + ammonia ($273 < T$ (K) < 333, $p < 40$ MPa): ○ Harms-Watzenberg [5].

Linear mixture model : Application

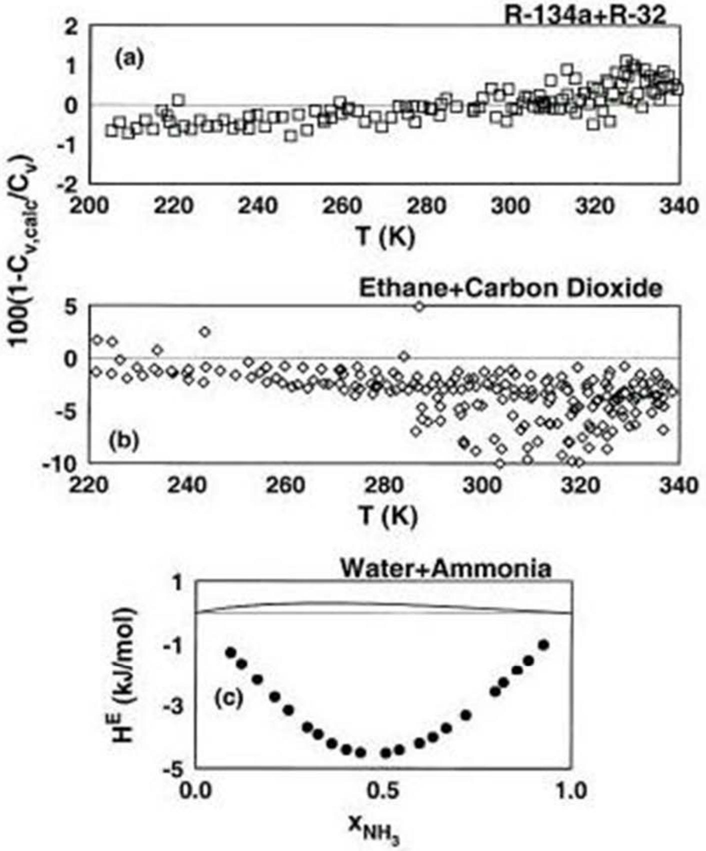

Fig. 3. Deviations between measured caloric properties and values calculated from the linear mixture model. (a) Liquid R-134a + R-32 C_V ($x \approx 0.5$): □ Magee and Haynes [15]. (b) Isochoric heat capacity for ethane + carbon dioxide: ◇ Magee [13]. (c) Excess enthalpy in liquid water + ammonia ($T = 298.15$ K, $p = 5$ MPa): ● Staudt [28].

Enhancement to the Mixture Model

- Modification of the reducing functions

$$T_n(\mathbf{x}) = \sum_{i=1}^{l}\sum_{j=1}^{l} x_i x_j T_{n,ij} \qquad T_{n,ij} = k_{T,ij}\frac{1}{2}\left(T_{n,ii} + T_{n,jj}\right)$$

$$V_n(\mathbf{x}) = \sum_{i=1}^{l}\sum_{j=1}^{l} x_i x_j V_{n,ij} \qquad V_{n,ij} = k_{V,ij}\frac{1}{2}\left(V_{n,ii} + V_{n,jj}\right)$$

  - $k_{T,ij}$, $k_{V,ij}$: adjustable parameter
  - Effect of varying $k_{T,ij}$, $k_{V,ij}$
    - ➔VLE of ethane+carbon dioxide (Fig.4) ($k_{T,ij} > k_{V,ij}$)
    - ➔C_v : 1.4% deviation (Fig.5)

Enhancement to the Mixture Model

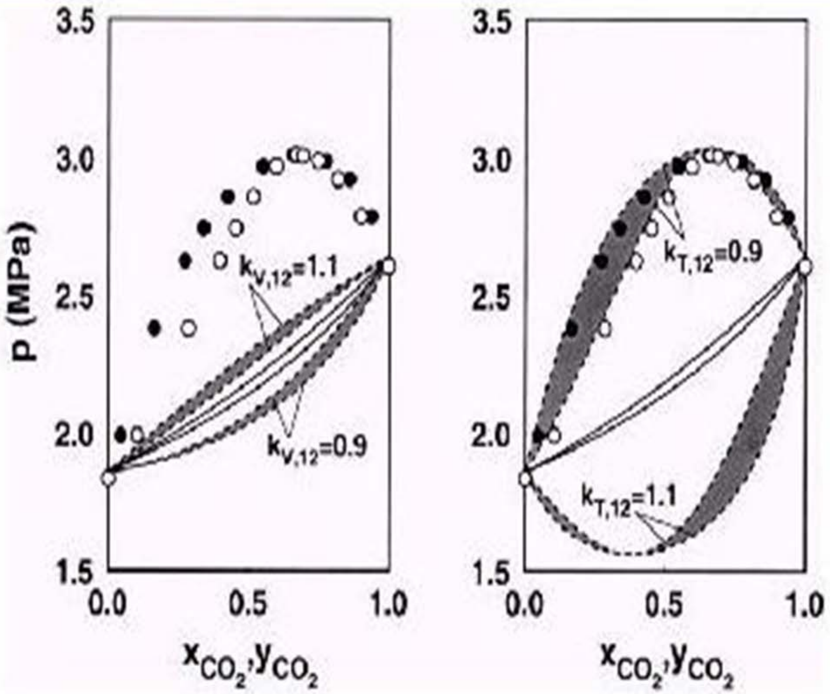

Fig. 4. Influence of the parameters $k_{T,12}$ and $k_{V,12}$ in the quadratic reducing function on the VLE of ethane + carbon dioxide: ○, ● Fredenslund and Mollerup [3]; solid line: $k_T = 1.0$, $k_V = 1.0$.

Enhancement to the Mixture Model

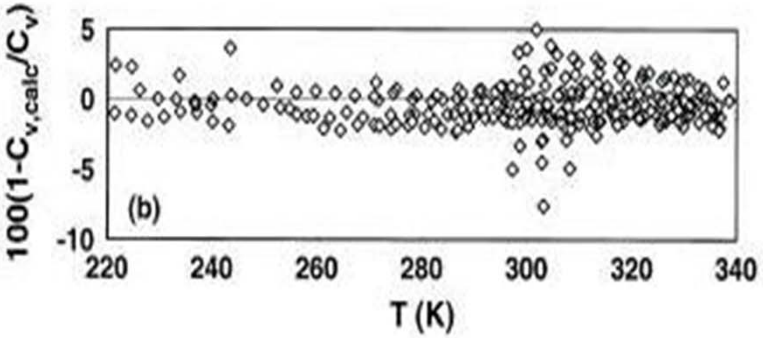

Fig. 5. Deviations between ethane + carbon dioxide isochoric heat capacities and values calculated from the Helmholtz energy model with $k_{T,12} = 0.9$: ◇ Magee [13].

Enhancement to the Mixture Model

- Modification by Tilner-Roth
  - supplement the quadratic expression with β_T, β_V

$$T_n(\mathbf{x}) = x_1^2 T_{n,1} + x_2^2 T_{n,2} + 2x_2(1 - x_2^{\beta_T})T_{n,12}$$

$$V_n(\mathbf{x}) = x_1^2 V_{n,1} + x_2^2 V_{n,2} + 2x_2(1 - x_2^{\beta_V})V_{n,12}$$

  - effect of exponents on the shape (Fig.6)
  - influence of $T_{\mathrm{n},12}$ or $V_{\mathrm{n},12}$
    - ➔asymmetric with respect to composition
  - Additional flexibility for tuning of the mixture model

Enhancement to the Mixture Model

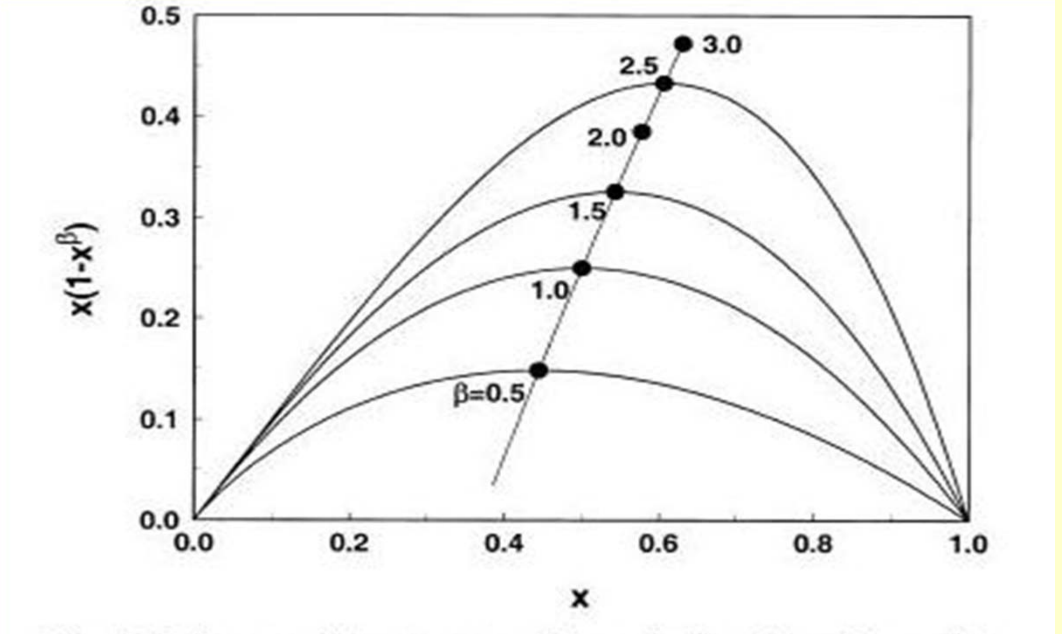

Fig. 6. Influence of the exponent β_T on the function $x(1-x^{\beta_T})$.

Enhancement to the Mixture Model

- Modification by Lemmon
  - ▶ modified the linear reducing function

$$T_n(\mathbf{x}) = \sum_{i=1}^{l} x_i T_{n,i} + \sum_{i=1}^{l-1} \sum_{j=i+1}^{l} x_i^{\beta_{ij}} x_j \zeta_{ij}$$

$$V_n(\mathbf{x}) = \sum_{i=1}^{l} x_i V_{n,i} + \sum_{i=1}^{l-1} \sum_{j=i+1}^{l} x_i x_j \xi_{ij}$$

  - ▶ $\zeta_{ij}, \xi_{ij}, \beta_{ij}$: modify the shape of the reducing parameter
  - ▶ $\beta_{ij}=1$, $\zeta_{ij} = \left(T_{n,i} + T_{n,j}\right)\left(k_{T,ij} - 1\right)$

$$\xi_{ij} = \left(V_{n,i} + V_{n,j}\right)\left(k_{V,ij} - 1\right)$$

➔for ethane+CO_2, ζ_{ij}=-67.4K ($k_{T,ij}$=0.89)

Departure function

- Departure function

$$\Delta\alpha^r(\tau,\delta,\mathbf{x}) = \sum_{i=1}^{l-1}\sum_{j=i+1}^{l} x_i x_j \Delta\alpha_{ij}(\tau,\delta,x_i,x_j)$$

  - ▶ only to mixture properties, no effect at the pure fluid limits
  - ▶ magnitude of departure function
    - ➔generally one order smaller than the residual α^r
  - ▶ modeling : regression analysis by Wagner
    - ➔a set of of experimental data→lowest standard deviation→bank of terms→subset of term for $\Delta\alpha_{ij}$
    - ➔optimization : modified Marquardt-Fletcher algorithm

Applications by Tillner-Roth

- Introduction an exponent γ in the departure function for a binary system

$$\Delta\alpha^{\mathrm{r}}(\tau,\delta,x) = x_2\left(1 - x_2^{\gamma}\right)\Delta\alpha_{ij}\left(\tau,\delta,x_i,x_j\right)$$

  - ➔asymmetric influence
  - ➔very effective for simple system, R-152+R134a
  - ➔reduce the number of terms in the departure function
  - ➔applied only to binary systems to date

- ▶ For water+ammonia,

$$x\delta^{n_k}\tau^{m_k}\exp\left(-\delta^{e_k}\right) \text{ and } x^2\delta^{n_k}\tau^{m_k}\exp\left(-\delta^{e_k}\right)$$

Applications by Tillner-Roth

- Results for R-134a+R-32
  - five-term departure function

$$\Delta\alpha^r(\tau,\delta,\mathbf{x}) = x(1-x^\gamma)\left[\sum_{k=1}^{2} c_k \delta^{n_k}\tau^{m_k} + \sum_{k=3}^{5} c_k \delta^{n_k}\tau^{m_k} \exp\left(-\delta^{e_k}\right)\right]$$

  - Fig.7 (cf. Fig.2b)
    - ➔density at liquid & vapor region : ±0.1%
    - ➔density at critical region : -6 ~ ±0.4%

Applications by Tillner-Roth

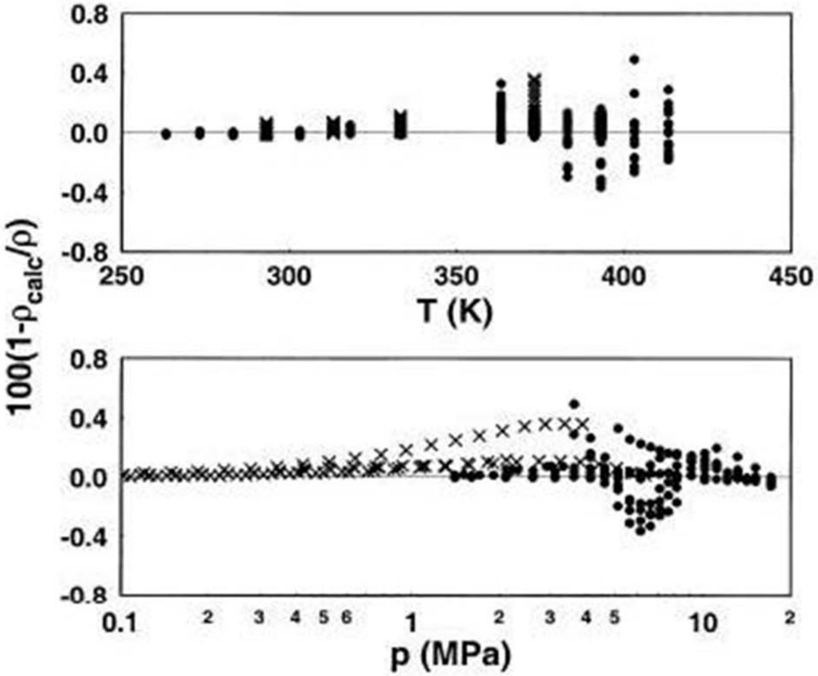

Fig. 7. Deviations between densities of R-134a + R-32 and values calculated from the Helmholtz energy model ($x \approx 0.5$): ● liquid densities of Kleemiss [9]; × vapor densities of Kleemiss [9].

Applications by Tillner-Roth

- Results for water+ammonia
  - ▶ 14-term departure function : 19 adjustable parameters

$$\frac{\Delta\alpha^{\mathrm{r}}(\tau,\delta,\mathbf{x})}{x\left(1-x^{\gamma}\right)}=c_1\delta^{n_1}\tau^{m_1}+\sum_{k=2}^{6}c_k\delta^{n_k}\tau^{m_k}\exp\left(-\delta^{e_k}\right)+x\sum_{k=7}^{13}c_k\delta^{n_k}\tau^{m_k}\exp\left(-\delta^{e_k}\right)$$

$$+c_{14}x^2\delta^{n_{14}}\tau^{m_{14}}\exp\left(-\delta^{e_{14}}\right)$$

  - ▶ Fig.8 (cf. Fig.1b, Fig.3c)
    - ➔improved representation

Applications by Tillner-Roth

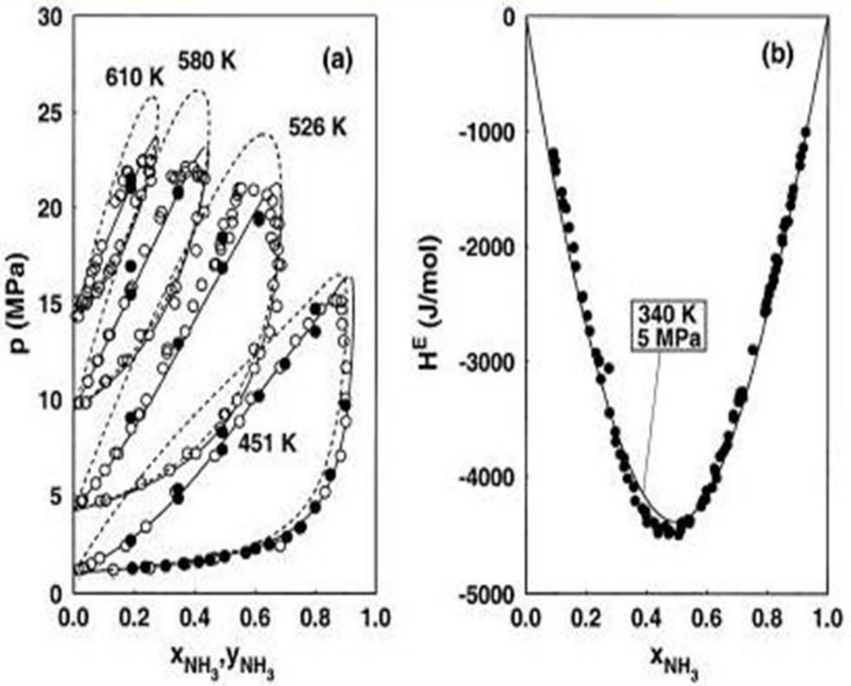

Fig. 8. Vapor–liquid equilibrium and excess enthalpy of water + ammonia. (a) VLE data: ○ Rizvi and Heidemann [21]; ○ Sassen et al. [24]. (b) Excess enthalpies ($298 < T$ (K) < 373, $5 < p$ (MPa) < 12): ● Staudt [28]; solid line: Helmholtz energy model including departure function; dashed line: linear mixture model.

Applications by Lemmon

- Generalized departure function

$$\Delta\alpha^{\mathrm{r}}(\tau,\delta,\mathbf{x})=\sum_{i=1}^{l-1}\sum_{j=i+1}^{l}x_i x_j F_{ij}\Delta\alpha_{ij}(\tau,\delta)$$

$$\Delta\alpha_{ij}(\tau,\delta)=\sum_{k=1}^{10}c_k\delta^{n_k}\tau^{m_k}$$

  - ▶ c_k, n_k, m_k : fixed the same for all mixture
  - ▶ F_{ij}, ζ_{ij}, ξ_{ij}, β_{ij} : adjustable parameters from (p,V,T,x)
    - ➔0.2% in density, 1% in heat capacities
    - ➔1-2% bubble point pressure at critical temp.
    - ➔5-10% bubble point pressure at critical temp. father apart

Applications by Lemmon

- Results
  - propane + *n*-butane : Fig.10
    - less than 0.04% average absolute deviation in density
    - 0.4% average absolute deviation in bubble point pressure
  - Uncertainty of the equation reported
    - 0.2% in density
    - 1% in heat capacities
  - Fig.11 : ternary refrigerant mixture

Applications by Lemmon

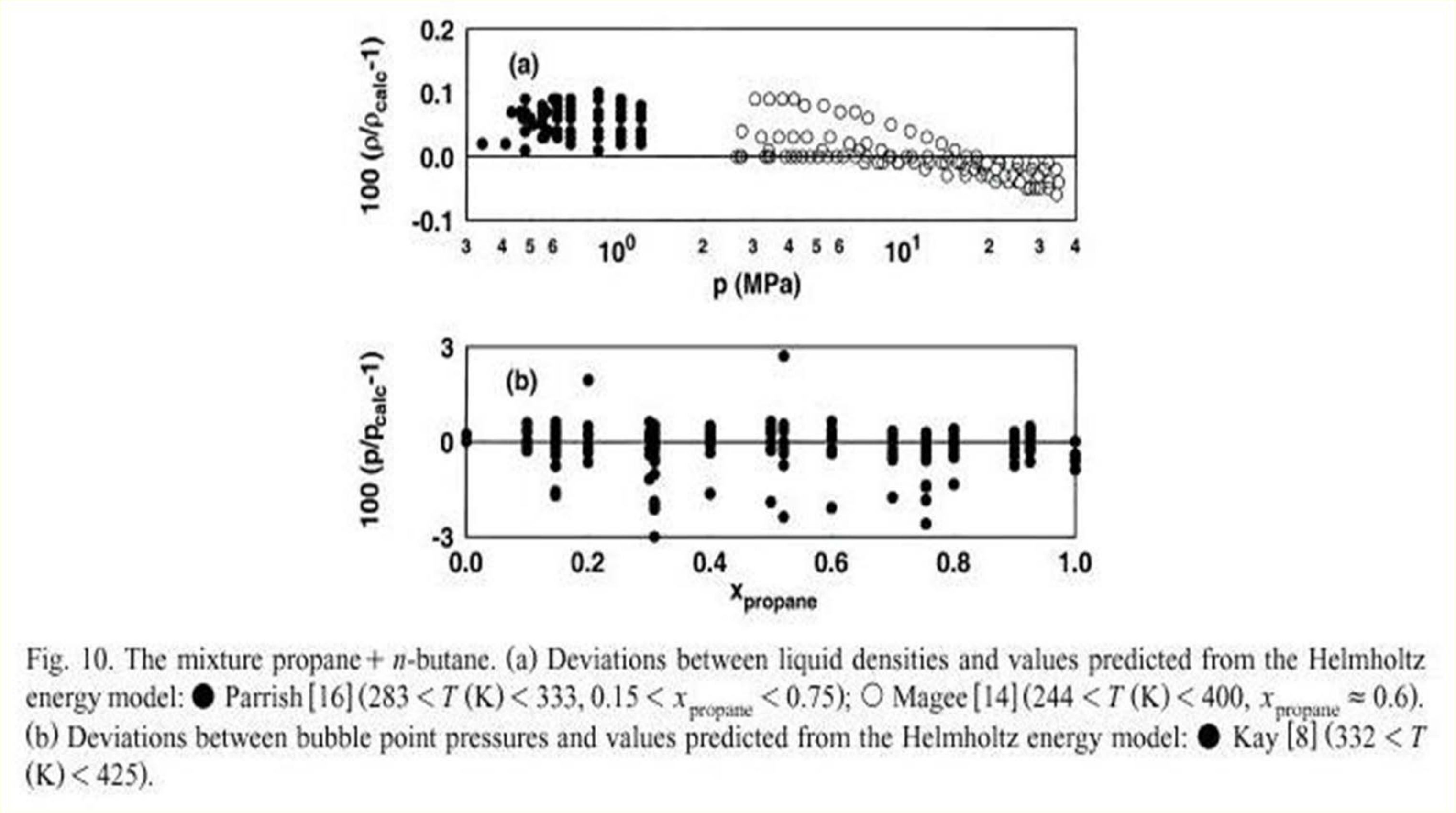

Fig. 10. The mixture propane + *n*-butane. (a) Deviations between liquid densities and values predicted from the Helmholtz energy model: ● Parrish [16] ($283 < T$ (K) < 333, $0.15 < x_{\text{propane}} < 0.75$); ○ Magee [14] ($244 < T$ (K) < 400, $x_{\text{propane}} \approx 0.6$). (b) Deviations between bubble point pressures and values predicted from the Helmholtz energy model: ● Kay [8] ($332 < T$ (K) < 425).

Applications by Lemmon

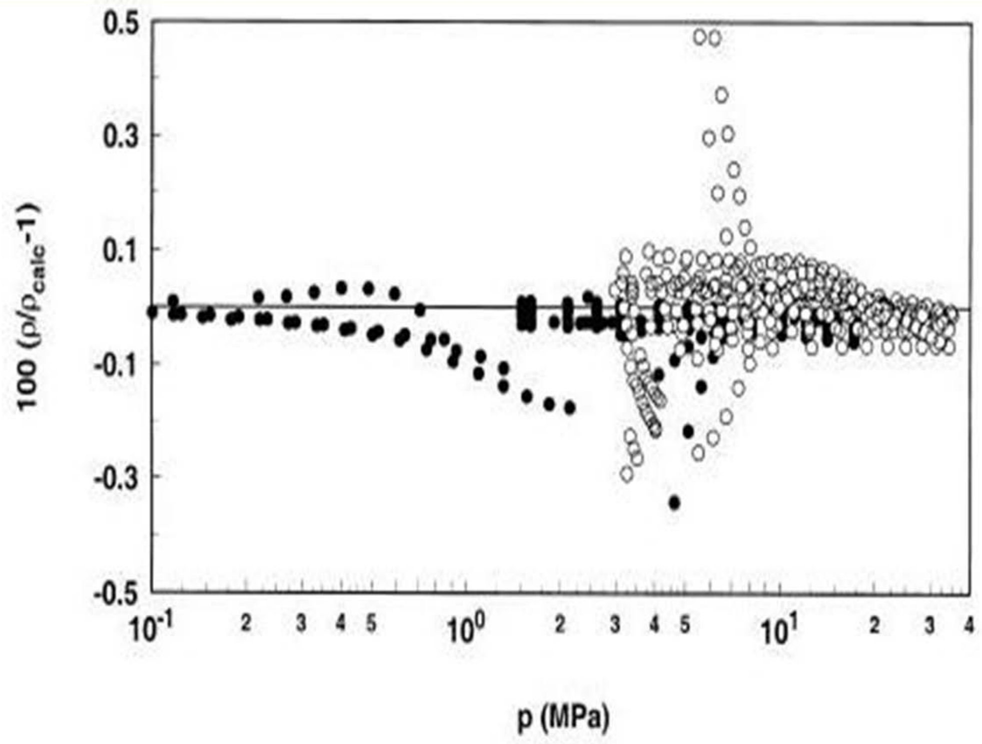

Fig. 11. Deviations between experimental densities for the ternary system R-134a + R-125 + R-32 and values predicted from the Helmholtz energy model: ● Kleemiss [9] ($243 < T$ (K) < 353); ○ Magee and Haynes [15] ($200 < T$ (K) < 400).

Conclusions

- EOS for mixture in terms of the Helmholtz energy has been developed and applied to several fluid systems by two different research groups
- By Tillner-Roth, model of single binary systems for which comprehensive accurate data are available
- By Lemmon, generalized model was presented which accurately predicts thermodynamic properties of mixtures
- Further research for more nonideal systems and complex multicomponent mixtures