Binary Mixtures In and Beyond the Critical Region: I. Thermodynamic Properties[1]

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ABSTRACT

An extended law of corresponding states in combination with a parametric crossover equation of state is applied to the prediction of thermodynamic properties and phase behavior of pure fluids and binary mixtures over a wide region around vapor-liquid critical points. For pure fluids, a generalized form of the model is given that requires only the acentric factor of the pure component. For mixtures, the critical locus is also required. A good representation of thermodynamic property data is achieved in the range of temperatures $0.8T_c(x) \leq T \leq 1.5T_c(x)$ and densities $0.35\rho_c(x) \leq \rho \leq 1.65\rho_c(x)$.

KEY WORDS: acentric factor; binary mixtures; critical region; equation of state; ethane, n-butane; phase behavior; R12; R22; R13B1; R114; thermodynamic properties.

1. INTRODUCTION

A new parametric crossover equation of state (EOS) for pure fluids and binary mixtures which reproduces scaling laws in the critical region and is transformed into a regular classical expansion far away from the critical point has been proposed recently by Kiselev et al. [1]-[4]. The equation for all mixtures in this model depends only on the parameters of the EOS for pure components, the critical locus, which can be obtained from the very accurate critical-region VLE correlations of Rainwater [5], and the excess critical compressibility factor ΔZ_c. Since the parameters for pure components were obtained in Refs. [1]-[4] from a fit of the crossover EOS to the PVT and sound velocity (or specific heat capacity) data, this approach also requires the highly accurate experimental data in and beyond the critical region of pure components.

In this paper we present a new model which extends the approach proposed by Kiselev et al. [1]-[4] to other fluids and fluid mixtures, and does not require any experimental data for pure components. All parameters of the crossover EOS for one-component fluids in our model depend only on the acentric factor ω, so that if the acentric factor is known, all other thermodynamic properties of pure components and binary mixtures can be predicted. We apply the model to ethane + n-butane, R22+R12 and R13B1+R114 systems, and compare with experimental data.

2. CROSSOVER FREE-ENERGY DENSITY

Let ρ be the density, T the temperature, and A the Helmholtz free energy per mole of a pure fluid. In addition, we define two "distances" from the critical point

$$\tau = \frac{T - T_c}{T_c}, \quad \Delta\rho = \frac{\rho - \rho_c}{\rho_c}, \tag{1}$$

where T_c is the critical temperature and ρ_c is the critical density. The isomorphic free-energy density of a binary mixture is given by [1]

$$\rho\tilde{A}(T, \rho, \tilde{x}) = \rho A(T, \rho, x) - \rho\tilde{\mu}x(T, \rho, \tilde{x}), \tag{2}$$

where $\tilde{\mu} = \mu_2 - \mu_1$ is the difference of the chemical potentials μ_1 and μ_2 of the mixture components, and $x = N_2/(N_1 + N_2)$ is the mole fraction of the second component

in the mixture. Based on the crossover equation of state for a pure fluid [1], the isomorphic free-energy density of binary mixtures reads

$$\begin{aligned}\frac{\rho\tilde{A}(T,\rho,\tilde{x})}{R\rho_{c0}T_{c0}} &= \tilde{k}r^{2-\alpha}R^{\alpha}(q)\Big[\tilde{a}\Psi_0(\theta)+\sum_{i=1}^{5}\tilde{c}_i r^{\Delta_i}R^{-\tilde{\Delta}_i}(q)\Psi_i(\theta)\Big] \\ &+ \sum_{i=1}^{4}(\tilde{A}_i+\frac{\rho}{\rho_{c0}}\tilde{m}_i)\tau^i(\tilde{x})-\frac{P_c(\tilde{x})}{R\rho_{c0}T_{c0}} \\ &+ \frac{\rho T}{\rho_{c0}T_{c0}}[ln(1-\tilde{x})+\tilde{m}_0], \end{aligned} \tag{3}$$

$$\tau=\frac{T-T_c(\tilde{x})}{T_c(\tilde{x})}=r(1-b^2\theta^2), \tag{4}$$

$$\Delta\rho=\frac{\rho-\rho_c(\tilde{x})}{\rho_c(\tilde{x})}=\tilde{k}r^{\beta}R^{-\beta+1/2}(q)\theta+\tilde{d}_1\tau, \tag{5}$$

where R is the universal gas constant, α,β and Δ_i are universal critical exponents, b^2 is a universal linear-model parameter. The universal scaled functions $\Psi_i(\theta)$ are the same as those in the parametric crossover model of Kiselev and Sengers [6], while the crossover function $R(q)=R(rg)$ (with g the inverse Ginzburg number) is defined by the expression given in Ref. [1]. For the system-dependent parameters $\tilde{d}_1(\tilde{x})$, $\tilde{k}(\tilde{x})$, $\tilde{a}(\tilde{x})$, $\tilde{c}_i(\tilde{x})$, $\tilde{g}(\tilde{x})$, $\tilde{m}_i(\tilde{x})$ and $\tilde{A}_i(\tilde{x})$, designated as $\tilde{k}_i$, as functions of the isomorphic variable $\tilde{x}$ we use the corresponding states relations employed earlier by Kiselev and Rainwater [2] in the extended law of corresponding states (LCS). In the context of the law of corresponding states these relations are universal for all binary mixtures with $\Delta Z_c \leq 0.2$.

3. ONE-COMPONENT FLUIDS

In the present paper, the parameters $\tilde{k}_i$ of pure components are represented as functions of the acentric factor ω. The asymptotic critical amplitude k and the inverse rescaled Ginzburg number g are written in the form

$$k_i(\omega)=a_{i(0)}(1+a_i^{(1)}\Delta\omega^{N_{k_i}}), \tag{6}$$

where $N_k=0.895$ and $N_g=0.5$. For all other coefficients we use

$$k_i(\omega)=a_{i(0)}+a_i^{(1)}\Delta\omega+a_i^{(2)}\Delta\omega^2+a_i^{(3)}\Delta\omega^3, \tag{7}$$

where $\Delta\omega = \omega - \omega_0$, and $a_{i(0)}$ and ω_0 are the parameters k_{i0} and the acentric factor of a reference system, respectively. In the present work, we choose methane as a reference system with $\omega_0 = \omega_{CH_4} = 0.011$ and parameters $a_{i(0)} = k_{i(CH_4)}$ obtained in Ref. [1]. Exponents N_k and N_g, the same as all other parameters in Eqs. (6) and (7) were obtained from a fit of Eqs.(3)-(5) together with Eqs. (6) and (7) to experimental PVT data for pure ethane [7], propane [8]-[10], n-butane [10, 11], benzene (recommended values) [12], carbon dioxide [13]-[15], and refrigerants R32 [16]-[18], R125 [19]-[21], and R134a [22]-[24] simultaneously in the range of temperatures and densities bounded by

$$\tau + 1.2\Delta\rho^2 \leq 0.5, \quad T \geq 0.995T_c. \tag{8}$$

We also used several additional PVT data for every substance, at subcritical conditions at the temperatures $0.85T_c \leq T \leq 0.98T_c$. In addition, the coefficients m_i for $i \geq 2$ which determine the background contributions to the isochoric specific heat were found from a fit of our crossover model to the sound-velocity data at near-critical isochores and temperatures $1.2T_c \leq T \leq 1.5T_c$ as calculated from high accuracy equations [25] for ethane, propane, n-butane and carbon dioxide, and from high accuracy equations of state [26] for R134a, and [27] for R32 and R125. The coefficients m_0 and m_1 were set equal zero.

The coefficients resulting from the fit are given in Table I. Figure 1 shows the percentage deviations of the experimental pressures from the calculated values as a function of temperature and density for different values of the acentric factor. Inside the region specified by Eq. (8), the deviations are within 1.5%, and increase to 3-5% at the boundary.

4. BINARY MIXTURES

In order to compare our model with experimental data for binary mixtures, we have chosen first the ethane + n-butane mixture where the critical locus is well known and the extended LCS equation of state already developed [2]. Figure 2 compares the values obtained from our model with the parameters k_{i0} and k_{i1} taken from Ref. [2] and those calculated from Eqs. (6) and (7) to the $PVT - x$ and VLE data of Kay

[11, 28]. One can see that both sets of the parameters k_{i0} and k_{i1} for pure components give essentially the same result for the binary mixture. The average deviation of the calculated pressures from the experimental data in the region given by Eq. (8) is about $2-3$ %, which approximately correspond to the accuracy achieved for pure ethane and n-butane with parameters given by Eqs. (6) and (7).

Our second example for pure fluids and binary mixtures is a comparison of theory and experiment for the mixtures of refrigerants R22 + R12 and R13B1 + R114 in the super- and subcritical regions. Since R12 ($\omega_{R12} = 0.1795$), R22 ($\omega_{R22} = 0.2208$), R13B1 ($\omega_{R13B1} = 0.171$), and R114 ($\omega_{R114} = 0.246$) were not used to develop Eqs. (6) and (7), this is a test of the predictive capability of the model. For the R22 + R12 mixture, we adopted the same critical locus as obtained by Higashi et al. [29]. A comparison with experimental data for pure R22 and for the R22 +R12 mixture is shown in Figs. 3 and 4. A good agreement with PVT-data and VLE data for the pure components and the binary mixture is observed. Since there is some inconsistency between the critical locus obtained by Higashi et al. [29] for the R13B1 + R114 mixture and experimental $PVTx$ data obtained by Hosotani et al. [38], we calculated the thermodynamic properties for this mixture with the critical locus reported by Higashi et al. [29] and also with the critical locus obtained by Rainwater and Lynch [39] from a fit of the modified Leung-Griffiths model to the experimental PTx-data of Hosotani et al. [38] (see Figs. 5 and 6). The calculations performed with the critical locus of Rainwater and Lynch [39] give a better representation of the $PVTx$ data [38], while the critical locus reported by Higashi et al. [29] gives a better result for the $T\rho x$ VLE data. Maximum deviations of about $5-6$% are observed between experimental data [38] and values of pressure calculated with the critical locus of Higashi et al. [29] in the one-phase region at high temperatures and densities at compositions $x = 0.1788$ and $x = 0.2719$ mole fraction of R114. For a better description of the $PVTx$ surface of R13B1 + R114 mixtures, a more accurate critical locus is needed.

5. CONCLUSIONS

We have presented a model for the prediction of the thermodynamic properties of binary mixtures that has scaling-law behavior in the critical region and that crosses over to mean-field behavior away from critical conditions. Unlike our previous model [1]-[4], this model does not require a preliminary fit to the experimental data for pure components. All system-dependent parameters for pure components can be calculated by using the acentric factor only. All other mixture parameters are obtained from generalized corresponding states relations based on the excess critical compressibility factor model developed in an earlier work [2]. The model can be applied to predict all thermodynamic one-phase and two-phase behavior, including PVTx and VLE behavior, in a region around the critical point. In order to extend our approach to the entire thermodynamic surface including the ideal gas limit, a crossover cubic equation of state can be used [41, 42].

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Table I: Constants in Eqs. (6) and (7).

k_i	$a_{i(0)}$	$a_i^{(1)}$	$a_i^{(2)}$	$a_i^{(3)}$
k	1.1504	0.3327	0	0
d_1	0.3196	-6.3148	6.2899	0
a	15.645	30.069	0	0
c_1	2.7515	69.602	-756.23	0
c_2	1.9267	-179.34	2964.7	0
c_3	-16.449	22.238	609.86	0
c_4	11.591	108.42	-931.57	0
c_5	0	391.82	-2082.9	0
g	1.7160	2.3583	0	0
A_1	-5.9352	-5.4426	2.2026	0
A_2	17.815	67.821	-311.07	0
A_3	3.0530	-62.559	267.70	0
m_2	-12.745	23.555	-1303.5	4019.1
m_3	1.3112	15.960	-536.01	1803.9
m_4	-0.4508	-3.9518	81.031	0

FIGURE CAPTIONS

Fig. 1. Percentage deviations of experimental pressures for pure ethane ($\omega_{C_2H_6} = 0.098$), propane ($\omega_{C_3H_8} = 0.150$), n-butane ($\omega_{C_4H_{10}} = 0.200$), benzene ($\omega_{BZN} = 0.212$), carbon dioxide ($\omega_{CO_2} = 0.225$), and refrigerants R32 ($\omega_{R32} = 0.277$), R125 ($\omega_{R125} = 0.303$) and R134a ($\omega_{R134a} = 0.325$), from values calculated with the crossover equation of state.

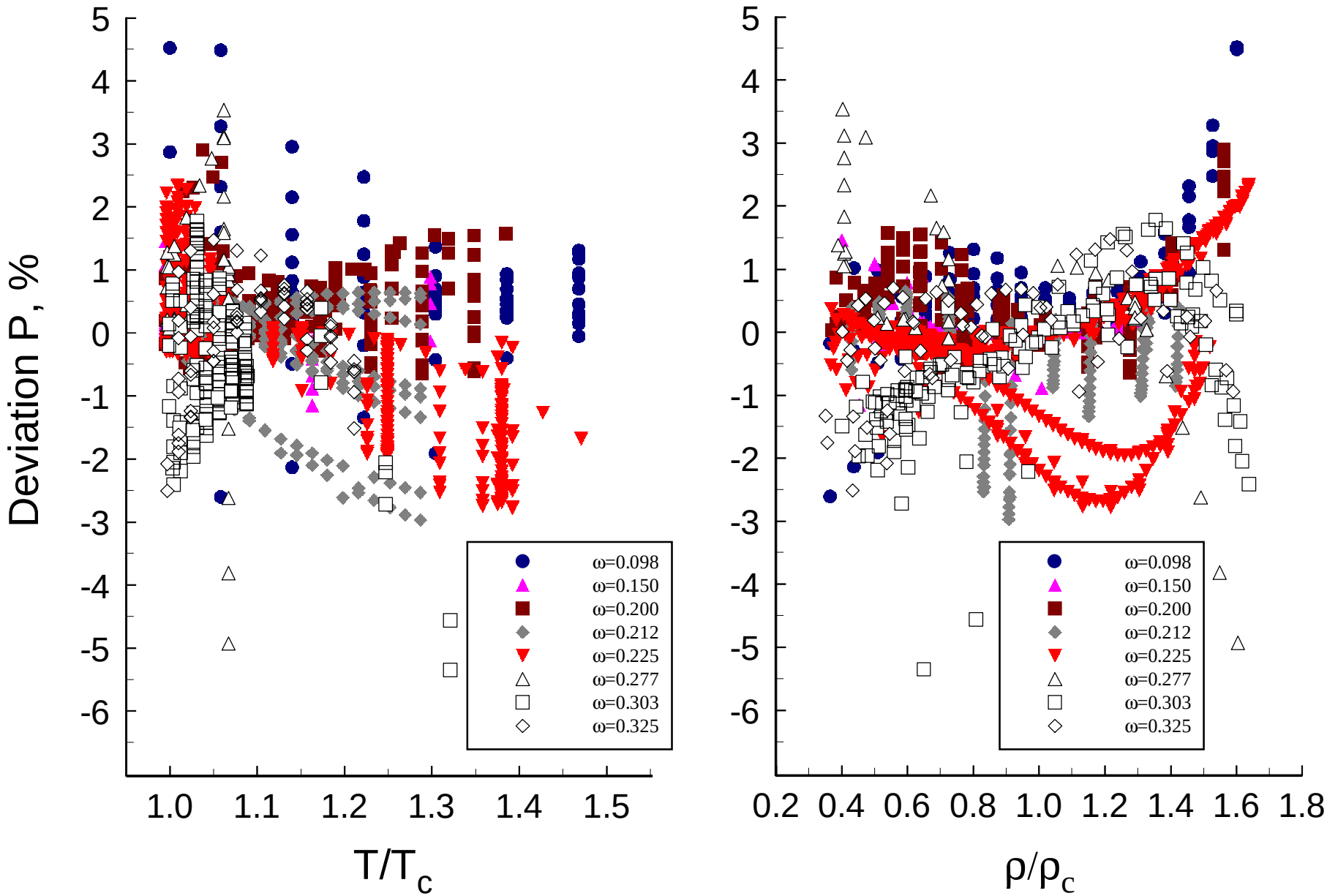
Fig. 2. $PVT - x$ and VLE data [11, 28] for ethane+n-butane mixtures at various concentrations of n-butane and predictions of the LCS model with parameters for pure components taken from Ref. [1] (solid curves) and calculated with Eqs. (6) and (7) (dashed curves).

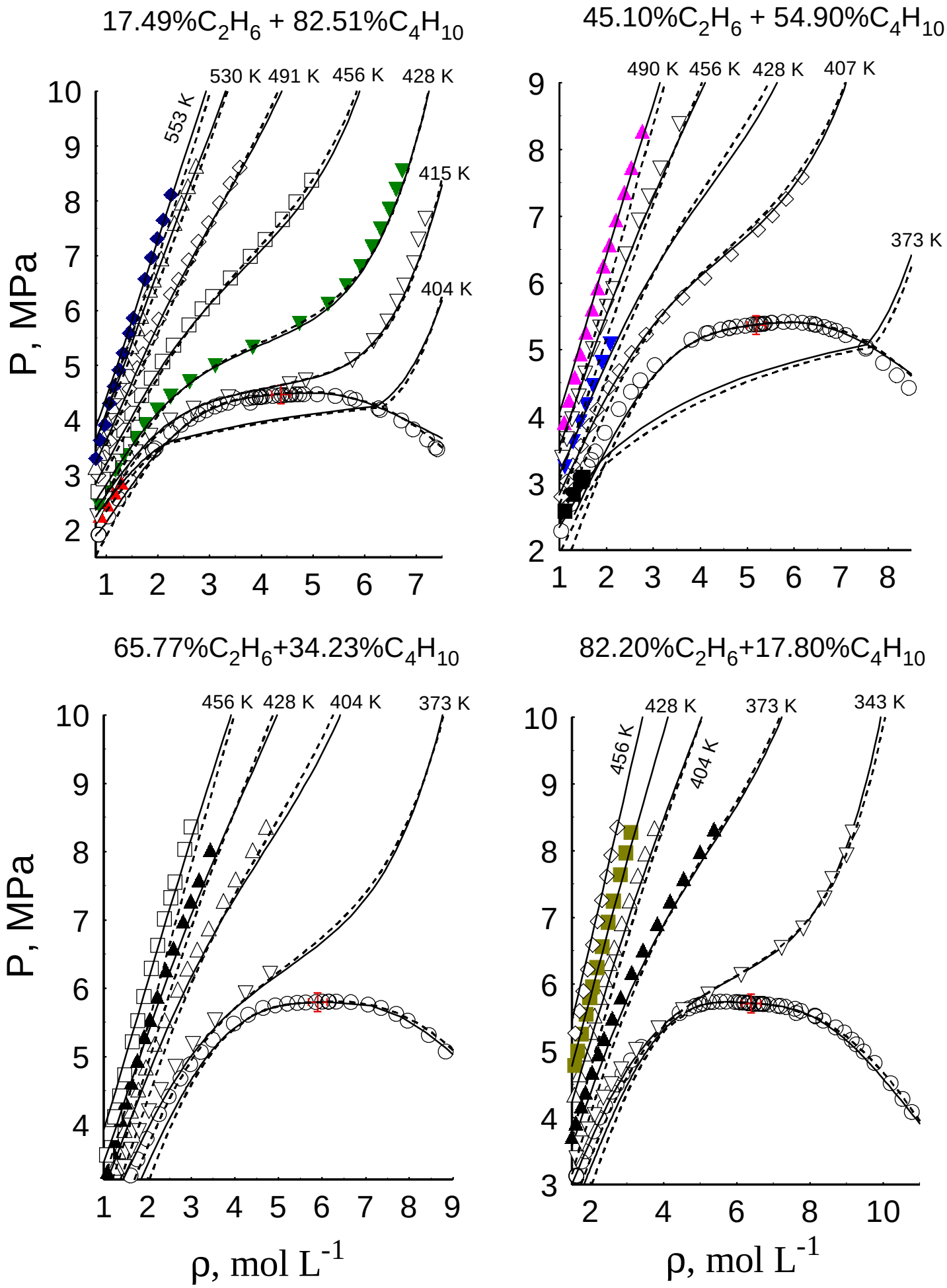
Fig. 3. PVT data for pure R12 and for the R22 + R12 mixture obtained by Takaishi et al. [30] with predictions of the crossover equation of state.

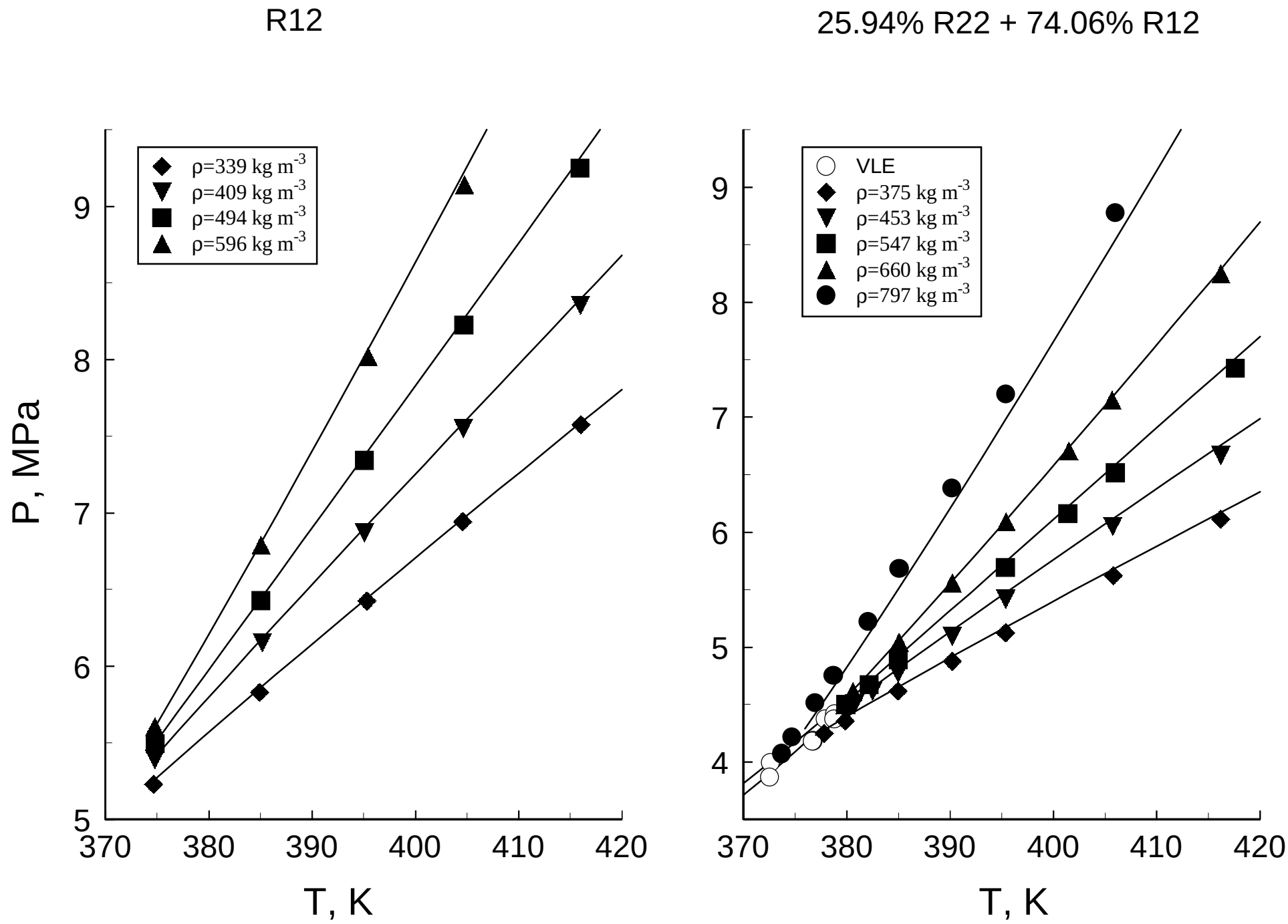
Fig. 4. VLE data for pure R12 [32]-[34] and R22 [35]-[37] (filled symbols), and for R22 + R12 mixtures [30, 31] (empty symbols) with predictions from the crossover model (curves).

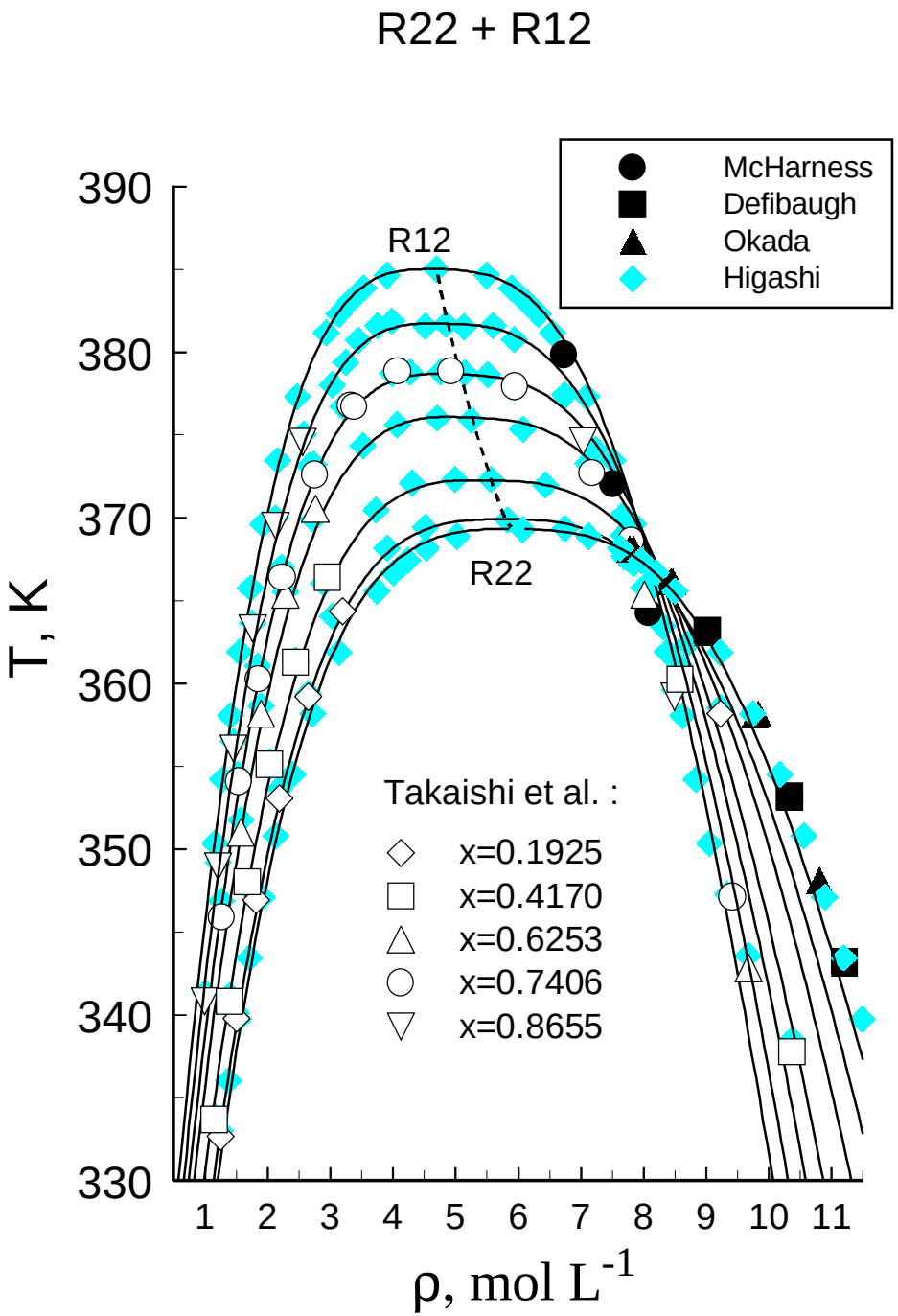
Fig. 5. PVT data for the R13B1 + R114 mixtures obtained by Hosotani et al. [38] with predictions of the crossover equation of state. Solid curves represent values calculated with the critical locus of Rainwater and Lynch [39] and dashed curves correspond to the critical locus of Higashi et al. [29].

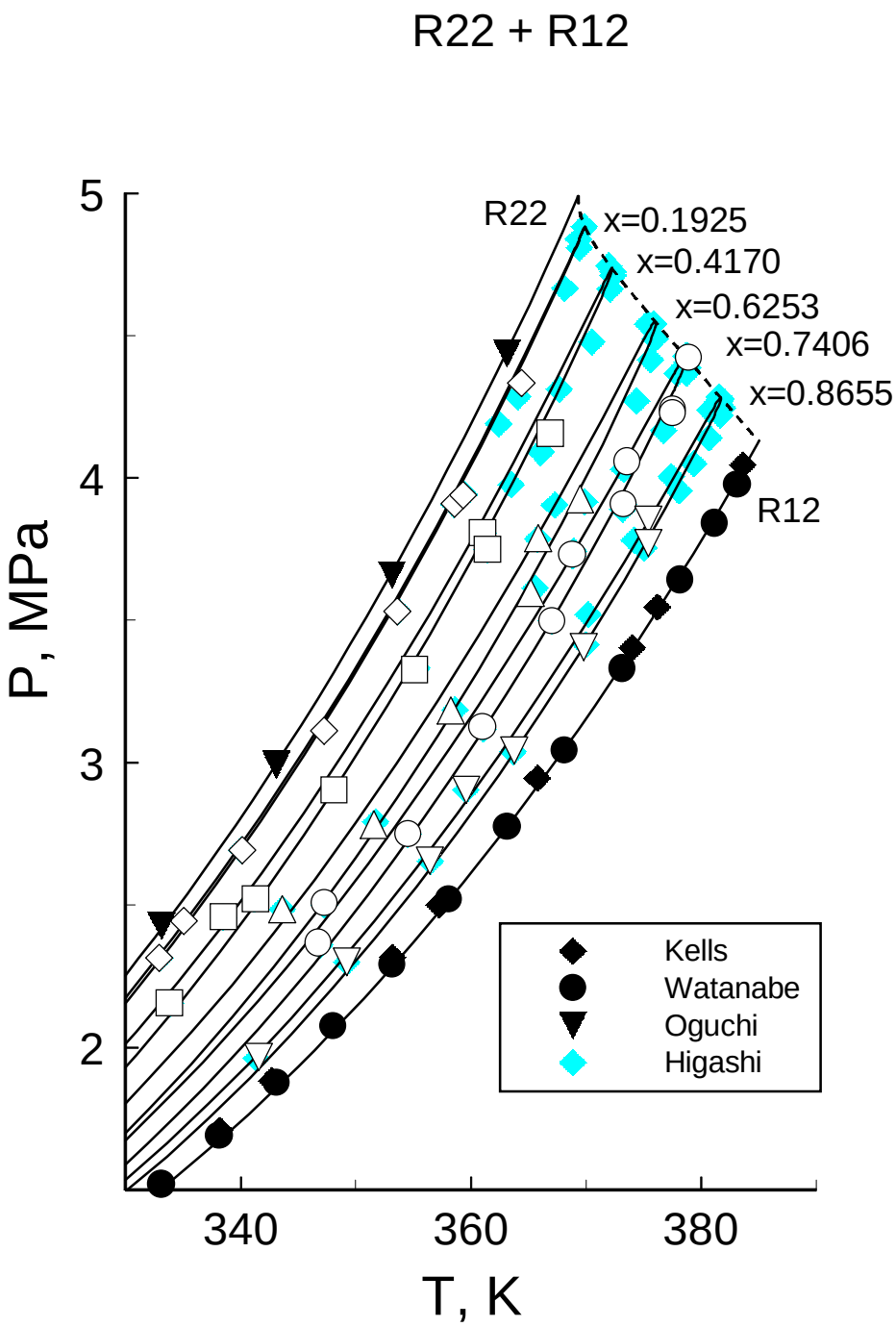
Fig. 6. VLE data for the R13B1 + R114 mixtures obtained by Hosotani et al. [38] (filled symbols) and by Higashi et al. [40] with predictions of the crossover equation of state. Solid curves represent values calculated with the critical locus of Rainwater and Lynch [39] and dashed curves correspond to the critical locus of Higashi et al. [29].

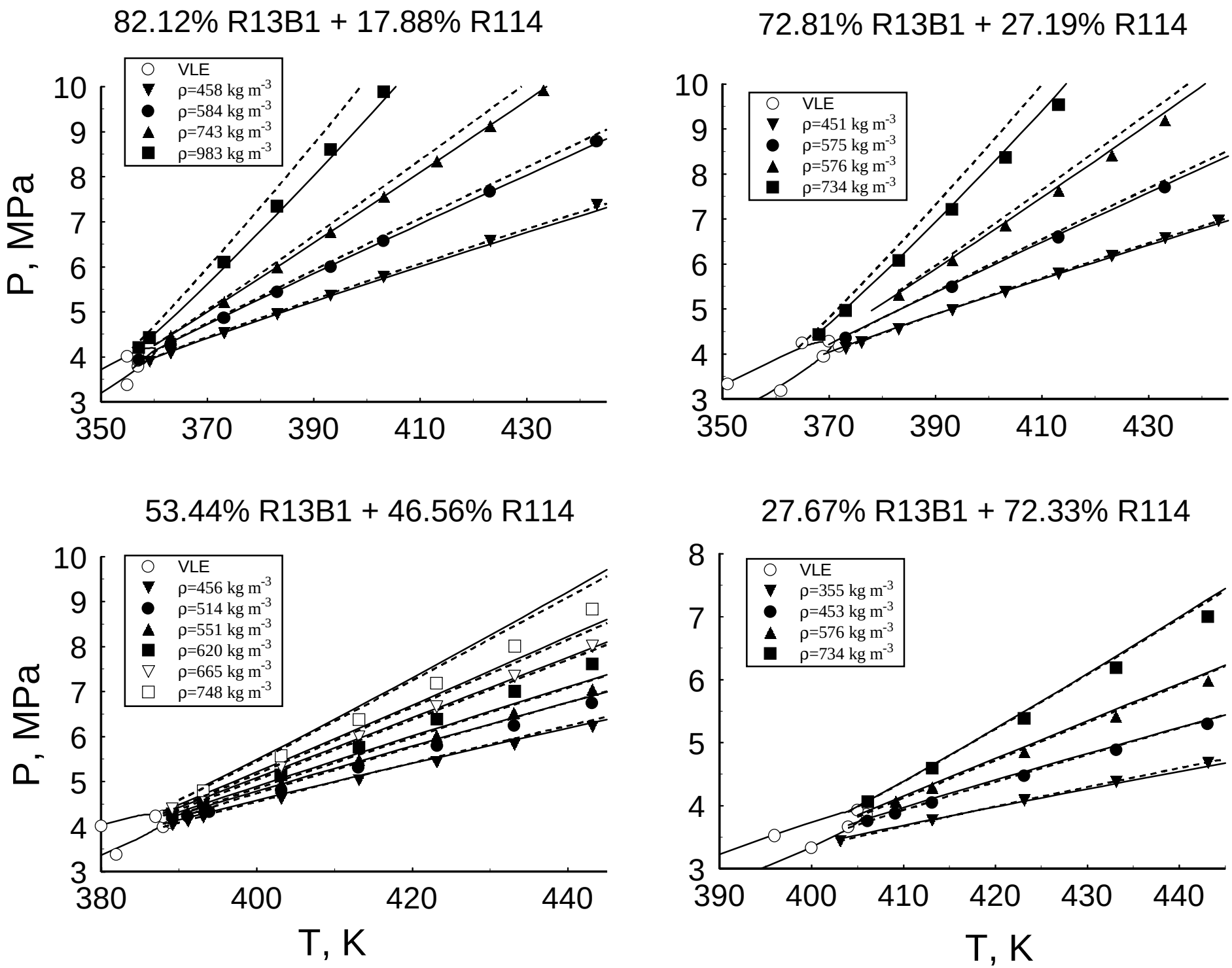

Deviation P, %
T/T$_c$
ρ/ρ$_c$
ω=0.098
ω=0.150
ω=0.200
ω=0.212
ω=0.225
ω=0.277
ω=0.303
ω=0.325

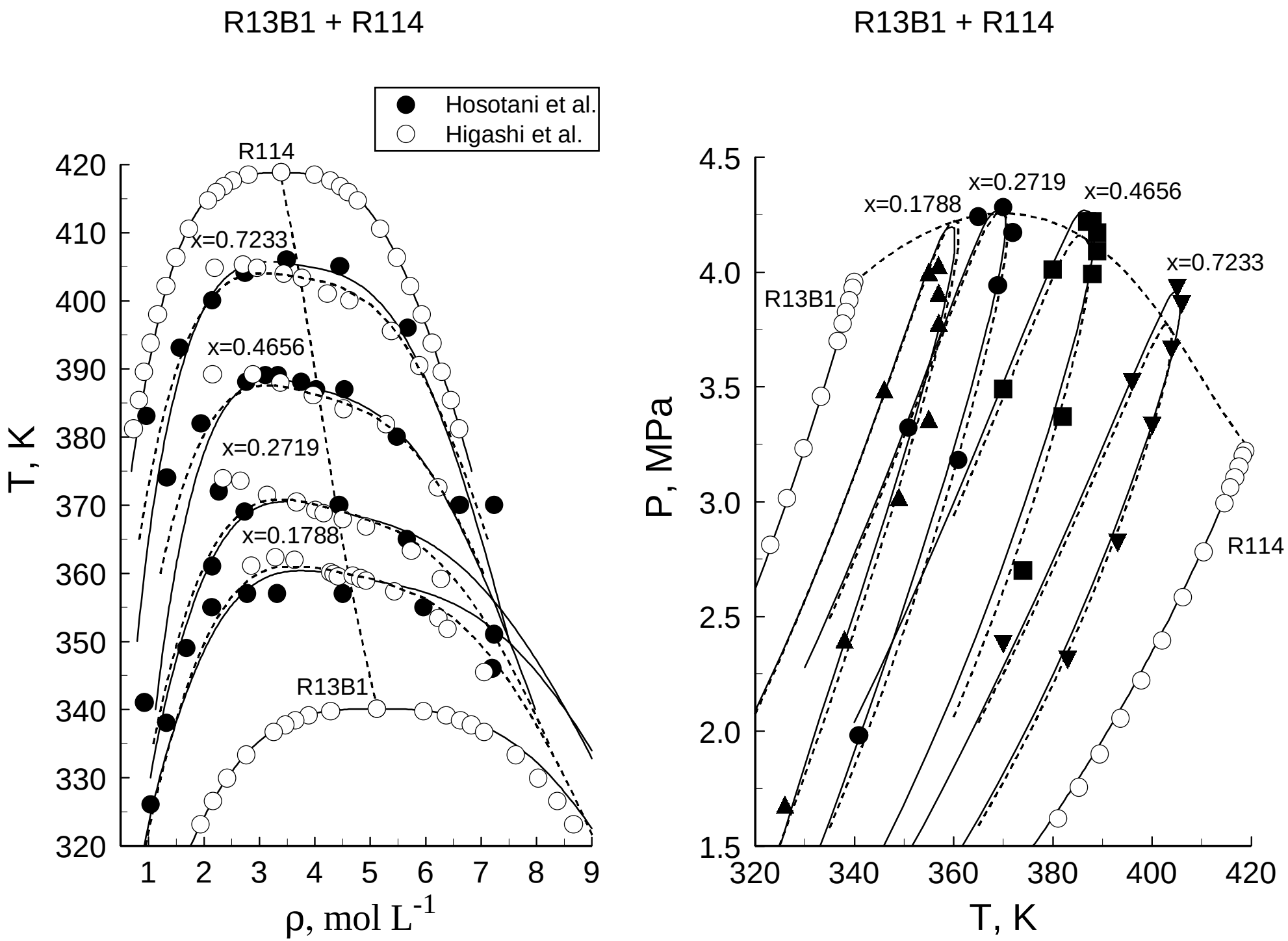

17.49%C2H6 + 82.51%C4H10
530 K
491 K
456 K
428 K
553 K
415 K
404 K
45.10%C2H6 + 54.90%C4H10
490 K
456 K
428 K
407 K
373 K
65.77%C2H6+34.23%C4H10
456 K
428 K
404 K
373 K
82.20%C2H6+17.80%C4H10
428 K
373 K
343 K
456 K
404 K
P, MPa
ρ, mol L-1


R12
25.94% R22 + 74.06% R12
ρ=339 kg m-3
ρ=409 kg m-3
ρ=494 kg m-3
ρ=596 kg m-3
VLE
ρ=375 kg m-3
ρ=453 kg m-3
ρ=547 kg m-3
ρ=660 kg m-3
ρ=797 kg m-3
P, MPa
T, K
T, K
5
6
7
8
9
4
370
380
390
400
410
420


R22 + R12
McHarness
Defibaugh
Okada
Higashi
R12
R22
Takaishi et al. :
x=0.1925
x=0.4170
x=0.6253
x=0.7406
x=0.8655
T, K
ρ, mol L-1
390
380
370
360
350
340
330
1
2
3
4
5
6
7
8
9
10
11


R22 + R12
R22
x=0.1925
x=0.4170
x=0.6253
x=0.7406
x=0.8655
R12
Kells
Watanabe
Oguchi
Higashi
P, MPa
T, K
5
4
3
2
340
360
380


82.12% R13B1 + 17.88% R114
VLE
ρ=458 kg m-3
ρ=584 kg m-3
ρ=743 kg m-3
ρ=983 kg m-3
P, MPa
72.81% R13B1 + 27.19% R114
VLE
ρ=451 kg m-3
ρ=575 kg m-3
ρ=576 kg m-3
ρ=734 kg m-3
53.44% R13B1 + 46.56% R114
VLE
ρ=456 kg m-3
ρ=514 kg m-3
ρ=551 kg m-3
ρ=620 kg m-3
ρ=665 kg m-3
ρ=748 kg m-3
P, MPa
T, K
27.67% R13B1 + 72.33% R114
VLE
ρ=355 kg m-3
ρ=453 kg m-3
ρ=576 kg m-3
ρ=734 kg m-3
T, K


R13B1 + R114
Hosotani et al.
Higashi et al.
R114
x=0.7233
x=0.4656
x=0.2719
x=0.1788
R13B1
T, K
ρ, mol L-1
R13B1 + R114
x=0.1788
x=0.2719
x=0.4656
x=0.7233
R13B1
R114
P, MPa
T, K